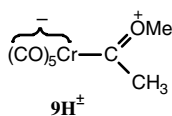
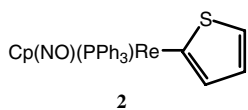


Chart 1.

while for the least acidic complexes (**12H–15H**) pK_a measurements were only feasible in pure acetonitrile [8,10]. For these latter carbene complexes pK_a values in 50% MeCN–50% water (v/v) were estimated as $pK_a^{50\% \text{ MeCN}} \approx pK_a^{\text{MeCN}} - 10.0$ [2].

The factors that are responsible for the wide range of pK_a values have been discussed in detail elsewhere [2] and hence only a brief summary is presented here.

- (1) The high acidity of **1H⁺–4H⁺** has been attributed to their cationic character combined with the fact that their conjugate bases are aromatic; for example, the conjugate base of **2H⁺**, **2**, is a thiophene derivative. The decrease in pK_a from 5.78 for **4H⁺** to 2.51 for **2H⁺** reflects an increase in aromatic stabilization in the order furan < selenophene < thiophene [3].

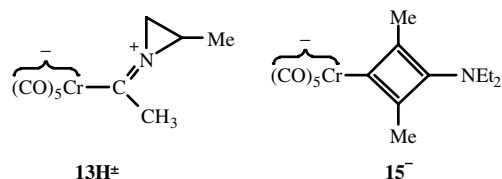


- (2) For the Cr(CO)₅ and W(CO)₅ complexes **5H–10H** the π -donor effect of the MeO vs. MeS (e.g., **9H⁺**) groups, and the effect of a phenyl group on the

α -carbon (**7H** and **8H**) are the main factors discriminating between the various complexes. Specifically, the stronger-donor effect of the MeO compared to that of the MeS group leads to stronger reactant stabilization of the methoxy carbene complexes, thereby increasing the pK_a (**10H** vs. **6H** and **9H** vs. **5H**), while the electron withdrawing inductive and resonance effects of the phenyl group increase the stability of the respective anions and reduce the pK_a (**7H** vs. **9H** and **8H** vs. **10H**).

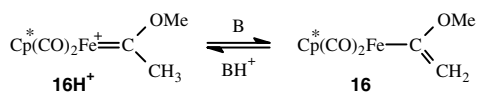
- (3) The much lower acidity of **11H** than that of **10H** reflects an enhanced stabilization of **11H** by the π -donor effect of the oxygen; this enhanced stabilization is the result of the cyclic structure of **11H** which locks the oxygen into a position for better π -overlap.
- (4) The higher pK_a of **12H** compared to that of **10H** is the result of replacing an electron-withdrawing CO ligand with the electron donating PPh₃.
- (5) The low acidity of **13H** and **14H** can be attributed to the π -donor effect of the amine substituents which is substantially stronger than that of a methoxy group. The reason why **13H** is more acidic than

14H is that here the π -donor effect of the nitrogen is reduced due to angle strain in the resonance structure **13H[±]** caused by the three-membered ring. In the case of **15H**, an important factor that makes this compound the least acidic carbene complex on the list is that the conjugate base **15⁻** is antiaromatic by virtue of being a cyclobutadiene derivative [10].



For **1H⁺**–**4H⁺** and **5H**–**11H** kinetic acidities in 50% MeCN–50% water (v/v) at 25 °C have also been determined by measuring proton transfer rates involving amine and carboxylate buffers [3–9]. Because the large differences in the pK_a values lead to large differences in the thermodynamics of the proton transfer, no meaningful direct comparisons of the rate constants for the various carbene complexes can be made. However, comparisons can be made by determining the *intrinsic* rate constants (k_0) for proton transfer which refer to the rate constants in the absence of a thermodynamic driving force and were obtained by suitable extrapolations or interpolations. The respective intrinsic rate constants involving primary aliphatic amines ($k_0^{\text{RNH}_2}$), secondary alicyclic amines ($k_0^{\text{R}_2\text{NH}}$) and carboxylate ions ($k_0^{\text{RCOO}^-}$) are summarized in Table 1. Their dependence on the various structural features of the carbene complexes is quite different from that of the pK_a values; this dependence will be scrutinized in Section 3.

In the present paper we report on an investigation of a Fischer carbene complex from a family for which neither thermodynamic nor kinetic acidities have been measured. It is the cationic (methoxymethylcarbene)dicarbonylpentamethylcyclopentadienyl iron complex **16H⁺**.



The results of this study complement those for the system summarized in Chart 1 and Table 1 and provides new insights into how structural factors affect pK_a values of Fischer carbenes and their intrinsic rate constants of proton transfer.

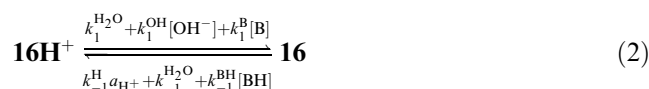
2. Results

2.1. General features and pK_a determinations

The triflate salt of **16H⁺** as well as its conjugate base, **16**, are quite stable in pure, dry acetonitrile but not in

aqueous acetonitrile where hydrolysis leads to rapid decomposition. UV/Vis spectra taken in pure acetonitrile are shown in Fig. 1. The first spectrum is that of **16H⁺**, the second that of **16** generated in the presence of 0.02 M triethylamine and the third that of the recovered **16H⁺** obtained after adding methanesulfonic acid to the solution of **16**. The virtually quantitative recovery of **16H⁺** indicates good reversibility of the proton transfer in acetonitrile.

Because of the rapid hydrolysis in 50% MeCN–50% water similar experiments which would allow a spectrophotometric pK_a determination could not be performed in this solvent. However, the pK_a of **16H⁺** was accessible from kinetic experiments carried out in a stopped-flow spectrophotometer. Proton transfer in buffered aqueous acetonitrile solutions involves three pathways as illustrated by Eq. (2). Under pseudo-first-order conditions, with the carbene complex



as the minor component, the observed pseudo-first-order rate constant for equilibrium approach is given by Eq. (3).

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

If k_{obsd} is determined as a function of increasing buffer base concentration at constant pH one obtains linear plots whose slopes are given by Eq. (4) where pK_a^{BH} is the pK_a of the buffer

$$\text{Slope} = k_1^{\text{B}} + k_{-1}^{\text{BH}} \frac{a_{\text{H}^+}}{K_a^{\text{BH}}} = k_1^{\text{B}} \left(1 + \frac{a_{\text{H}^+}}{K_a^{\text{CH}}} \right), \quad (4)$$

acid, pK_a^{CH} that of the carbene complex.












Fig. 2 shows such plots determined in morpholine buffers at different pH values. From a plot of the slope vs. a_{H^+} (Fig. 3) a $k_1^{\text{B}} = (3.08 \pm 0.03) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ and $K_a^{\text{CH}} = (5.65 \pm 0.22) \times 10^{-9} \text{ M}$ ($pK_a = 8.25 \pm 0.02$) was obtained. Furthermore, a value of $1.04 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for k_{-1}^{BH} could be calculated as $k_1 K_a^{\text{BH}} / K_a^{\text{CH}}$. Similar experiments with methoxyethylamine (plots not shown) yielded $k_1^{\text{B}} = (6.27 \pm 0.03) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $K_a^{\text{CH}} = (5.80 \pm 0.20) \times 10^{-9} \text{ M}$ ($pK_a = 8.24 \pm 0.02$) and $k_{-1}^{\text{BH}} = 4.40 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. Note that the close agreement between the two pK_a values shows excellent internal consistency although the fact that the values are virtually identical is fortuitous.

2.2. Kinetics in KOH solutions

Experiments were conducted at seven $[\text{KOH}]$ ranging from 0.005 to 0.05 M. In this range the $k_1^{\text{OH}^-} [\text{OH}^-]$ term

Table 1

Intrinsic rate constants for proton transfer from Fischer carbene complexes to primary aliphatic amines (RNH₂), secondary alicyclic amines (R₂NH) and carboxylate ions (RCOO⁻) in 50% MeCN–50% water (v/v) at 25 °C

Carbene complex		pK _a	log k ₀ ^{RNH₂}	log k ₀ ^{R₂NH}	log k ₀ ^{RCOO⁻}
	(2H ⁺) ^a	2.51	0.27	1.05	1.21
	(3H ⁺) ^b	4.17	0.14	0.92	0.72
	(4H ⁺) ^a	5.78	-0.83	-0.46	-0.01
	(16H ⁺) ^c	8.25	2.64	2.99	3.42
	(5H) ^d	8.37	2.17	2.50	2.27
	(6H) ^d	9.05	2.09	2.61	2.17
	(7H) ^e	10.18	1.55	1.93	
	(8H) ^f	10.40	1.51	1.86	0.79
	(9H) ^e	12.36	2.73	3.18	
	(10H) ^f	12.50	3.04	3.70	
	(11H) ^g	14.47		3.51	

^a Ref. [3].^b Ref. [4].^c This work.^d Ref. [5].^e Ref. [7].^f Ref. [6].^g Ref. [9].

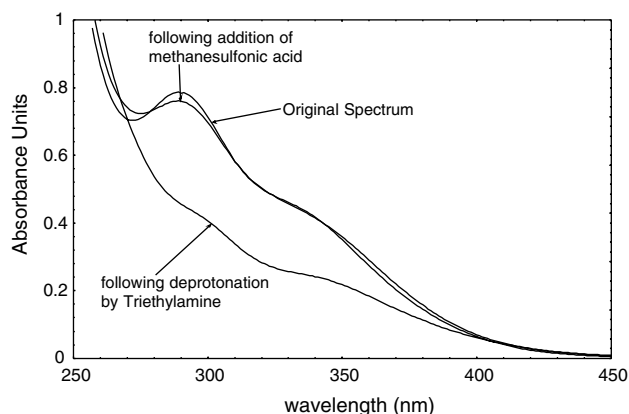


Fig. 1. UV-Vis spectrum of $16H^+$ in acetonitrile at 25 °C. Deprotonation of the substrate and recovery of original spectrum also included.

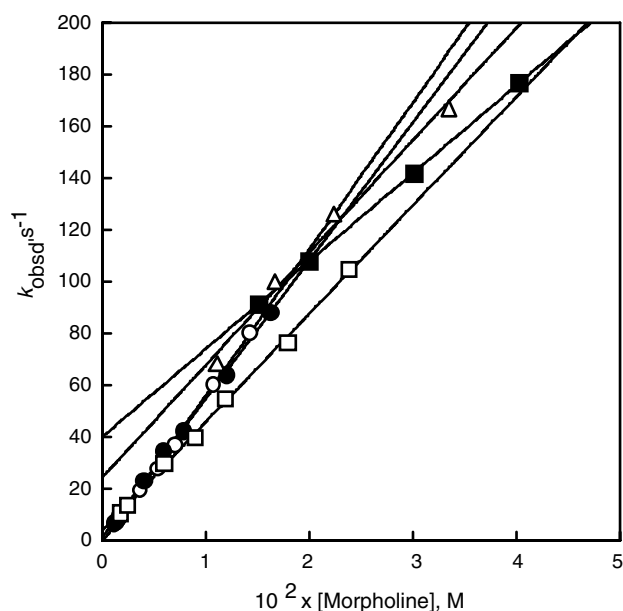


Fig. 2. Kinetics of the reaction of $16H^+$ with morpholine buffers: \circ (pH 8.32), \bullet (pH 8.39), \square (pH 8.63), \blacksquare (pH 9.33), \triangle (pH 9.64).

in Eq. (3) is dominant and a plot of k_{obsd} vs. $[\text{KOH}]$ (not shown) yielded $k_1^{\text{OH}} = (1.84 \pm 0.08) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

2.3. Kinetics in amine and carboxylate buffers

In addition to the kinetic determinations of the pK_a^{CH} in morpholine and methoxyethylamine buffers, rates were also measured in *n*-butylamine, aminoacetonitrile, glycnamide, piperidine, piperazine, 1-(2-hydroxyethyl) piperazine (HEPA), acetate, methoxyacetate, and chloroacetate buffers; attempts at measuring rates in buffers more acidic than chloroacetic acid were unsuccessful because they were too fast for the stopped-flow technique. These experiments were performed at a pH close to the respective pK_a^{BH} values. All plots of k_{obsd} vs. buffer base

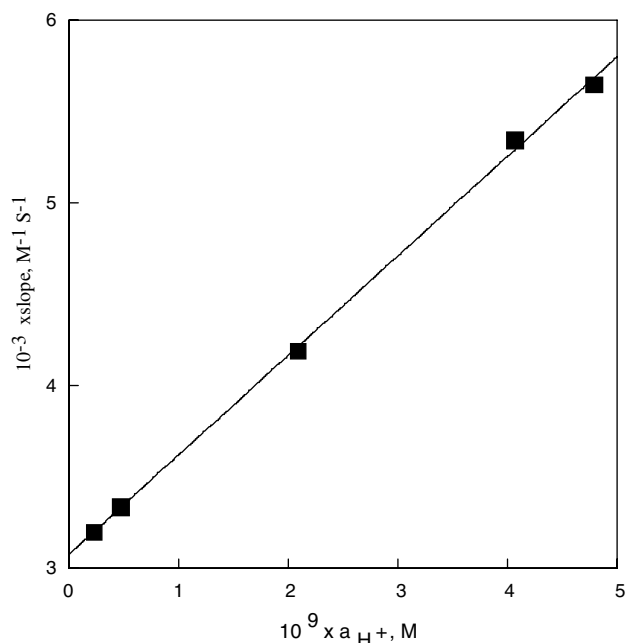


Fig. 3. Dependence of slope on a_{H^+} according to Eq. (4) for the reaction of $16H^+$ with morpholine.

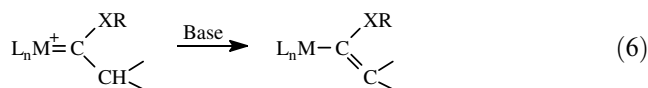
concentrations at seven concentrations were strictly linear with small intercepts. The slopes are again given by Eq. (4) while the k_1^{B} values were obtained by solving Eq. (5).

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

3. Discussion

3.1. Acidity of $16H^+$

The pK_a of $16H^+$ is 8.25. This makes $16H^+$ more acidic than any of the *neutral* carbene complexes (**5H–15H**) but less acidic than the four *cationic* carbene complexes ($1H^+–4H^+$) in Chart 1. The fact that the cationic carbene complexes are more acidic than the neutral ones implies that $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}^+$ and $\text{Cp}^*(\text{CO})_2 \text{Fe}^+$ moieties are stronger π acceptors than the $(\text{CO})_5\text{Cr}$ or $(\text{CO})_5\text{W}$ moieties. This is so despite the fact that the latter have five electron withdrawing CO ligands on the metal while the former only have one NO or two CO electron withdrawing ligands combined with some electron releasing groups (Cp, PPh_3 , Cp^*). Apparently the positive charge plays a dominant role; this is perhaps best understood in terms of the respective conjugate bases where for the cationic complexes the dominant resonance structure of the conjugate base is a neutral molecule (Eq. (6)) which gives it exceptional stability.



A major reason why, among the cationic carbene complexes, $1\text{H}^+ - 4\text{H}^+$ are considerably more acidic than 16H^+ is the extra stabilization enjoyed by the respective conjugate bases, **1–4**, by virtue of being aromatic. In fact, as pointed out in Section 1, the acidity order of the monocyclic derivatives, $2\text{H}^+ > 3\text{H}^+ > 4\text{H}^+$, reflects the trend in the aromatic stabilization energies, thiophene > selenophene > furan [11–13], and supports the notion that the aromaticity of the conjugate bases is an important acidity enhancing factor [3].

The different ligands are expected to influence the acidities of the cationic carbene complexes as well, but it is not clear which carbene complexes benefit the most. What seems to favor the iron carbene complex is the fact it has *two* electron withdrawing ligands (CO) and only one strong electron donating one (Cp*), while the rhenium derivatives have only one electron withdrawing ligand (NO) and two electron donating ligands (Cp, strong; PPh₃, weak). However, the NO group which carries a formal positive charge [14] is much more electron withdrawing than the CO group and this may more than offset the advantage of having two CO groups. As discussed below, the lower intrinsic rate constants for $1\text{H}^+ - 4\text{H}^+$ compared to 16H^+ strongly supports this notion.

4. Rate constants

Table 2 summarizes the rate constants for deprotonation of 16H^+ and protonation of **16**. Fig. 4 shows statistically corrected Eigen plots [15] from which the Brønsted coefficients (β and α) and $\log k_0$ were determined; the latter refers to the points of intersection of the plots of $\log(k_1^B/q)$ and $\log(k_{-1}^{BH}/p)$ vs. $pK_a^{BH} - pK_a^{CH} + \log p/q$. The β , α and $\log k_0$ values are reported in Table 3.

Table 2

Rate constants for proton transfer between 16H^+ ($pK_a^{CH} = 8.25 \pm 0.02$) and various bases in 50% MeCN–50% water (v/v) at 25 °C, $\mu = 0.1$ M (KCl)

Base	pK_a^{BH}	$k_1^B \text{ M}^{-1} \text{ s}^{-1}$	$k_{-1}^{BH} \text{ M}^{-1} \text{ s}^{-1}$
OH ⁻	16.64	$(1.84 \pm 0.08) \times 10^4$	$(2.11 \pm 0.19) \times 10^{-3b}$
Piperidine	11.01	$(7.51 \pm 0.05) \times 10^4$	$(1.31 \pm 0.13) \times 10^2$
Piperazine	9.97	$(1.56 \pm 0.02) \times 10^4$	$(2.97 \pm 0.18) \times 10^2$
HEPA ^a	9.33	$(6.51 \pm 0.09) \times 10^3$	$(5.41 \pm 0.32) \times 10^2$
Morpholine	8.72	$(3.07 \pm 0.06) \times 10^3$	$(1.04 \pm 0.07) \times 10^3$
<i>n</i> -BuNH ₂	10.40	$(2.62 \pm 0.04) \times 10^4$	$(1.85 \pm 0.07) \times 10^2$
MeOCH ₂ CH ₂ NH ₂	9.39	$(6.26 \pm 0.22) \times 10^3$	$(4.53 \pm 0.37) \times 10^2$
H ₂ NCOCH ₂ NH ₂	8.14	$(2.59 \pm 0.12) \times 10^2$	$(3.34 \pm 0.31) \times 10^2$
NCCH ₂ NH ₂	5.29	$(1.19 \pm 0.03) \times 10^1$	$(1.08 \pm 0.08) \times 10^4$
CH ₃ COO ⁻	5.93	$(1.68 \pm 0.02) \times 10^2$	$(3.51 \pm 0.20) \times 10^4$
MeOCH ₂ COO ⁻	4.73	$(3.10 \pm 0.06) \times 10^1$	$(1.03 \pm 0.07) \times 10^5$
ClCH ₂ COO ⁻	3.94	$(1.21 \pm 0.05) \times 10^1$	$(2.47 \pm 0.22) \times 10^5$

^a 1-(2-hydroxyethyl)piperazine.

^b In units of s⁻¹.

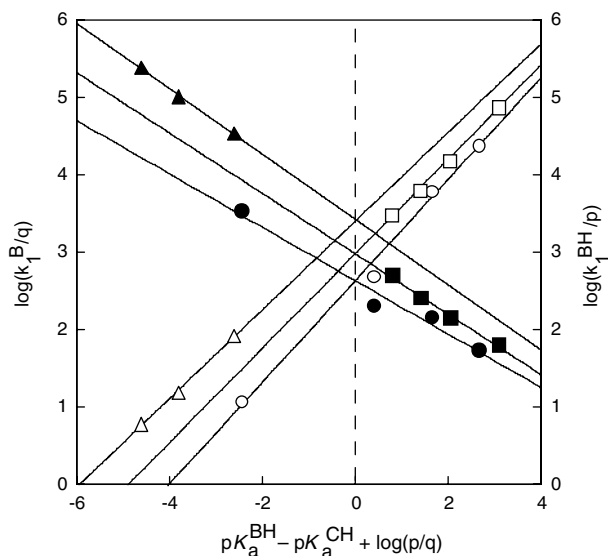


Fig. 4. Eigen plots for the reaction of 16H^+ with primary aliphatic amines (○, ●), alicyclic secondary amines (□, ■) and carboxylate ions (△, ▲). The points where the lines for $\log(k_1^B/q)$ and $\log(k_{-1}^{BH}/p)$ intersect correspond to $\log k_0$.

Table 3

Brønsted parameters for the deprotonation of 16H^+ ($pK_a = 8.25 \pm 0.02$)

Base type	β^a	α^b	$\log k_0^c$
RNH ₂	0.66 ± 0.04	0.34 ± 0.04	2.64 ± 0.08
R ₂ NH	0.61 ± 0.02	0.39 ± 0.02	2.99 ± 0.04
RCOO ⁻	0.58 ± 0.03	0.42 ± 0.03	3.42 ± 0.10

^a $d \log k_1^B / dpK_a^{BH}$.

^b $d \log k_{-1}^{BH} / d \log K_a^{BH}$.

^c $\log k_0 = \log k_1^B / q = \log k_{-1}^{BH} / p$ when $pK_a^{BH} - pK_a^{CH} + \log(p/q) = 0$.

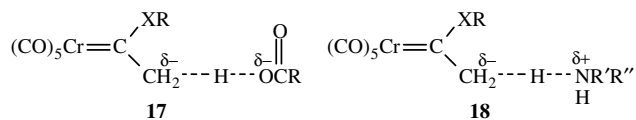
4.1. Intrinsic rate constants

4.1.1. Dependence on buffer

As is typically the case with intrinsic rate constants for proton transfers from carbene complexes (Table 1)

as well as from carbon acids in general [16–18], the k_0 values for 16H^+ show some dependence on the buffer type. Specifically, for 16H^+ , they increase in the order $\log k_0^{\text{RNH}_2} < \log k_0^{\text{R}_2\text{NH}} < \log k_0^{\text{RCOO}^-}$ (Table 3). The somewhat higher intrinsic rate constants for the secondary compared to the primary amines (Tables 1 and 3) is a well-known phenomenon caused by differences in the solvation energies of the respective protonated amines and the fact that the transition state solvation of the incipient protonated amine lags behind proton transfer [19,20]. In the absence of steric hindrance, the differences between $\log k_0^{\text{R}_2\text{NH}}$ and $\log k_0^{\text{RNH}_2}$ is typically around 0.8–1.0 [18,21]. For 16H^+ , this difference is only about 0.35 which indicates the presence of a moderate steric effect. When steric hindrance is severe, there may be a reversal in the order, i.e., $\log k_0^{\text{R}_2\text{NH}} < \log k_0^{\text{RNH}_2}$ [18,22,23].

The intrinsic rate constant for the carboxylate ions is larger than those for the amines (Table 3). This result follows the pattern of the cationic rhenium carbene complexes 2H^+ – 4H^+ (Table 1) but contrasts with that for the neutral carbene complexes where $\log k_0^{\text{R}_2\text{NH}} > \log k_0^{\text{RCOO}^-}$. These patterns can be understood in terms of electrostatic effects at the transition state. For the neutral carbene complexes the repulsive electrostatic interaction between the partial negative charges in **17** reduces $\log k_0^{\text{RCOO}^-}$ while the stabilizing electrostatic interaction between



the opposite charges in **18** increases $\log k_0^{\text{RNH}_2}$ and $\log k_0^{\text{R}_2\text{NH}}$. For the cationic carbene complexes 2H^+ – 4H^+ and 16H^+ , the overall positive charge on the carbene complex residue of the transition state apparently leads to a stabilizing interaction with the attacking anionic carboxylate ion (enhances $\log k_0^{\text{RCOO}^-}$) but a destabilizing interaction with the incipient positive charge on the amine nitrogen (reduces $\log k_0^{\text{RNH}_2}$ and $\log k_0^{\text{R}_2\text{NH}}$). Similar electrostatic effects have been reported for other reactions [24–26].

4.1.2. Dependence on carbene complex

When compared with other carbene complexes (Table 1), the $\log k_0$ values for the deprotonation of 16H^+ are quite high, much higher than for the other cationic complexes (1H^+ – 4H^+) and only slightly lower than for the alkylalkoxy carbene complexes 9H – 11H . In order to rationalize this finding one needs to analyze the various factors that influence intrinsic rates of proton transfer from carbon acids in general and from carbene complexes in particular.

The most important *general* factor is the degree of charge delocalization/resonance stabilization in the conjugate base of a carbon acid: the greater the delocalization/resonance the higher the intrinsic barrier or the lower the intrinsic rate constant [16–18]. The reason for this is that the transition state of these reactions is invariably imbalanced in the sense that resonance development lags behind proton transfer. As a result the resonance stabilization of the transition state is disproportionately weak compared to that of the fully formed carbanion which depresses the intrinsic rate constant and the more so the greater the resonance stabilization of the conjugate base. This behavior is an example of a much more general phenomenon known as the Principle of Nonperfect Synchronization (PNS); this principle states that whenever in a reaction the development of a product-stabilizing factor (in our case resonance) lags behind the main bond changes (in our case proton transfer), there is an increase in the intrinsic barrier or a reduction in the intrinsic rate constant [16–18]. The same is true when the loss of a reactant stabilizing factor is ahead of the main bond changes.

The fact that most proton transfers from carbon acids are much slower than those from normal acids [15] is a direct consequence of the PNS effect of the π -acceptor groups that stabilize the carbanions. Along with the nitroalkanes, the Fischer carbene complexes are among the carbon acids with the lowest k_0 values for proton transfer [1,2] reflecting the powerful π -acceptor effect of the metal moiety in these complexes.

Even though as a class all Fischer carbene complexes undergo relatively slow proton transfers, there are substantial differences in the individual $\log k_0$ values which, e.g. using secondary alicyclic amines as the proton acceptor, range from ~ -0.46 to ~ 3.70 . Obviously, individual structural features of these complexes can have a significant influence on k_0 . For example, the lower $\log k_0$ value for **7H** (1.93) compared to that of **9H** (3.18), or the lower $\log k_0$ value for **8H** (1.86) compared to that of **10H** (3.70) can be attributed to the additional resonance stabilization of **7** and **8**, respectively, by the phenyl group which contributes its own k_0 -reducing PNS effect [6]. This additional resonance stabilization is also the main reason why **7H** is more acidic than **9H** and **8H** more acidic than **10H** by about 2 $\text{p}K_a$ units.

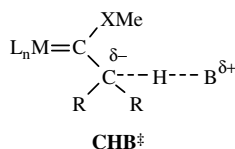
The even lower $\log k_0$ values for 1H^+ – 4H^+ have also been explained by the particularly strong resonance stabilization of the respective conjugate bases [3,4]. Here the source of the extra strong stabilization is the fact that the acids are cationic and hence the main resonance structure of the respective conjugate bases are stable neutral molecules (Eq. (6)). However, the fact that $\log k_0$ for 16H^+ is not similarly reduced, even though the dominant resonance structure of its conjugate base is also a stable neutral molecule, suggests that one or more additional factors come into play. One such factor is the NO ligand

in $1\text{H}^+ - 4\text{H}^+$; as noted in our discussion of the $\text{p}K_{\text{a}}$ values, its powerful π -acceptor effect is probably stronger than the combined effect of the two CO ligands in 16H^+ and enhances the resonance stabilization of the respective conjugate bases **1–4** further relative to that of **16**.

Another potential factor that emanates from the acid form rather than its conjugate base is the influence of the π -donor group attached to the carbene carbon and the degree of resonance stabilization that results from the push–pull effect with the π -acceptor; this push–pull effect will depend on the strength of both the π -donor and π -acceptor. It is reasonable to assume that the push–pull resonance behaves in a similar way as resonance effects in general, i.e., its loss at the transition state is ahead of the proton transfer. According to the PNS [16–18] this implies a lowering of the intrinsic rate. Inasmuch as the π -acceptor strength of the $\text{Re}(\text{Cp})(\text{NO})(\text{PPh}_3)$ moiety is stronger than that of the $\text{Fe}(\text{CO})_2(\text{PPh}_3)$ moiety one expects the intrinsic rate constants for the rhenium carbene complexes to show a greater reduction than that for 16H^+ . This effect probably contributes to the large differences in the $\log k_0$ values between the iron and rhenium carbene complexes.

The identity of the π -donor atom (O, Se, S) in the rhenium derivatives also affects their intrinsic rate constants [3]. For the latter complexes, the fact that **1–4** are derivatives of aromatic heterocycles complicates the picture. In fact aromaticity in the conjugate base leads to an increase in the intrinsic rate constant, as seen in the order $\text{S} > \text{Se} > \text{O}$ for $\log k_0$ of $2\text{H}^+ - 4\text{H}^+$, which reflects the increase in aromaticity of thiophene > selenophene > furan [11–15].

When no aromaticity is involved, other factors associated with the identity of the π -donor group dominate, as can be seen by comparing **5H** ($\log k_0 = 2.50$) with **9H** ($\log k_0 = 3.18$), or **6H** ($\log k_0 = 2.61$) with **10H** ($\log k_0 = 3.70$): the lower values for the MeS derivatives have been attributed to a combination of larger size of the MeS group, which leads to a more crowded transition state, and its weaker electron withdrawing [5] inductive effect. The inductive effect of the MeX group tends to increase the intrinsic rate constant because the substituent is closer to the site of negative charge development at the transition state (CHB^\ddagger) than in the delocalized



conjugate base (C^- , Eq. (1) and hence its stabilizing effect on the transition state is disproportionately large compared to that on the conjugate base. As a result there is greater enhancement of k_0 for the methoxy relative to the methylthio carbene complexes. Whether the

weaker π -donor effect of the MeS group enhances or reduces the differences in the $\log k_0$ values between **5H** and **9H** or between **6H** and **10H** could not be established with certainty [5].

Finally, the identity of the metal needs to be considered. Comparison of **9H** with **10H** shows a slight increase in $\log k_0$ when the $(\text{CO})_5\text{W}$ moiety is changed in to a $(\text{CO})_5\text{Cr}$ moiety, indicating that a change of the metal within the same group of the Periodic Table can affect the intrinsic rate constants. However, when comparing **5H** with **6H** or **7H** with **8H** the differences in $\log k_0$ virtually disappear. On the other hand the change from Fe(II) (group 8B) to Re(I) (Group 7B) constitute a more profound change than from the W(O) to Cr(O). Whether this change could potentially add significantly to the difference in the $\log k_0$ values between the iron and rhenium carbene complexes is unclear at this point.

5. Experimental section

5.1. Materials

$[\text{Cp}^*(\text{CO})_2\text{Fe}=\text{C}(\text{OMe})\text{Me}][\text{CF}_3\text{SO}_3]$ was prepared as described by Lapinte et al. [27]. ^1H NMR (CDCl_3) δ 4.62 (s, 3H, OMe), δ 3.05 (s, 3H, Me), δ 1.85 (s, 15H, Cp^*), in complete agreement with the literature values. The solvents and buffers used for this study were obtained from the same sources and purified in the same manner as described before [4].

5.2. Kinetic measurements

The determination of the $\text{p}K_{\text{a}}^{\text{CH}}$ of 16H^+ was approached by applying a kinetic method where data was obtained by stopped-flow spectrophotometry in the sequential mixing mode. In these experiments equal volumes of a blank solution containing the carbene in acetonitrile in one syringe and 0.2 M KCl in water in a second syringe were mixed after firing the first pneumatic drive. Following a 20 ms delay, the second drive was fired so that the first mixture was combined with buffer solution in 50:50 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ at $\mu = 0.1$ M and loss of carbene was monitored at 290 nm. The same technique was used for the reactions with buffers that had a $\text{p}K_{\text{a}}^{\text{BH}} < \text{p}K_{\text{a}}^{\text{CH}}$. With the more basic buffers single-mixed stopped-flow methodology was used. For these experiments one syringe was filled with buffer solution ($\mu = 0.2$ M in water only) while the other syringe was charged with substrate in acetonitrile. As with the sequential mixing experiments, all buffers and blank solutions were mock-mixed to determine actual pH of the reaction environment. In most cases k_{obsd} values were determined at seven buffer concentrations spanning a 10–20-fold range. The experiments were performed on

a Applied Photophysics DX.17MV stopped-flow spectrophotometer while spectra were taken with a Hewlett-Packard 8453 Agilent UV–Vis spectrophotometer. pH measurements were performed 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 [28].

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