Physical Organic Chemistry of Transition Metal Carbene Complexes. 14.[1] Thermodynamic Acidity Measurements of Fischer Carbene Complexes in Acetonitrile

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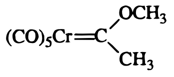
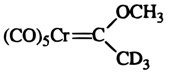
Abstract: The pK_a values of five Fischer carbene complexes of the general structure $(CO)_5Cr{=}C(OR)CHR'R''$, of two $(CO)_4(PR_3)Cr{=}C(OCH_3)CH_3$ type complexes and of one aminocarbene complex, $(CO)_5Cr{=}C(NCH(CH_3)CH_2)CH_3$, were determined in acetonitrile by a spectrophotometric method. These pK_a values span a range from 22.2 for $(CO)_5Cr{=}C(OCH_3)CH_3$ to 27.6 for $(CO)_5Cr{=}C(NCH(CH_3)CH_2)CH_3$. Deprotonation of the carbene complexes was achieved with strong amine bases such as TMG, DBU, and BEMP. Attempts at measuring the pK_a of some other carbene complexes failed either because of instability of the respective anions (e.g., $(CO)_5Cr{=}C(OCH_3)CH(CH_3)_2$) or because the p$K_a$ was too high for deprotonation to occur ($(CO)_5Cr{=}C(N(CH_3)_2)CH_3$). Similarities and differences in the structural dependence of these acidities in acetonitrile compared to other solvents such as 50% acetonitrile−50% water, DMSO, and THF are discussed.

Introduction

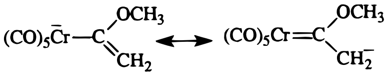
Fischer carbene complexes that contain one or several hydrogen atoms on the α-carbon (carbon adjacent to the carbene carbon) are moderately acidic. A prototypical example is pentacarbonyl(methoxymethylcarbene)chromium(0), **1-Cr**. The first indication that **1-Cr** has acidic properties was Kreiter's[2] observation of the rapid conversion of **1-Cr** into **1-Cr-d$_3$** in dilute $NaOCH_3/CH_3OD$ solutions. Casey and Anderson[3] subsequently showed that in THF solution the acidity of **1-Cr** is approximately the same as that of *p*-cyanophenol, an acid whose pK_a in water is 7.97. In quoting this work, numerous authors have, rather misleadingly, referred to **1-Cr** as an acid with a pK_a of 8; this, of course, cannot be correct since *p*-cyanophenoxide ion and **1-Cr**$^-$ should respond quite differently to a solvent change from THF to water. Ion-pairing effects in THF add further complications to a precise definition of acidity in this solvent. The pK_a of **1-Cr** in *water* was reported to be 12.3.[4]



1-Cr



1-Cr-d$_3$



1-Cr$^-$

pK_a measurements of Fischer carbene complexes in aqueous solutions are not straightforward because of rapid decomposition of the conjugate anion which, e.g. in the case of **1-Cr**$^-$, leads to acetaldehyde and $(CO)_5CrOH^-$ in a multistep process.[5] Hence such pK_a determinations have to be performed kinetically in a double-mixing stopped-flow spectrophotometer[6] by measuring k_1^{OH} and $k_{-1}^{H_2O}$ (in aqueous KOH) or k_1^{B} and k_{-1}^{BH} (in buffered solutions) according to eq 1. The acidity constant of the carbene complex, K_a^{CH}, is then obtained via eq 2 or 3 where K_w is the ionic product of the solvent and K_a^{BH} is the acidity constant of the buffer acid BH. Using this methodology, pK_a^{CH} values for a variety of carbene complexes such as **1-Cr**,[7] **1-Mo**,[8] **1-W**,[8] **2-Cr**,[7] **2-W**,[8] **3-Cr**,[8] **4-Cr**,[9] **5-Cr**,[1] **6-Cr**,[10] and **7-Cr**[10] have been

$$\mathbf{1\text{-}Cr} \underset{k_{-1}^{H_2O} + k_{-1}^{BH}[BH]}{\overset{k_1^{OH}[OH^-] + k_1^{B}[B]}{\rightleftharpoons}} \mathbf{1\text{-}Cr}^- \qquad (1)$$

$$K_a^{CH} = \frac{k_1^{OH}}{k_{-1}^{H_2O}} K_w \qquad (2)$$

$$K_a^{CH} = \frac{k_1^{B}}{k_{-1}^{BH}} K_a^{BH} \qquad (3)$$

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† University of California.

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[1] Part 13: Bernasconi, C. F.; Leyes, A. E.; García-Río, L. *Organometallics*. In press.

[2] Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390.

[3] Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.

[4] Gandler, J. R.; Bernasconi, C. F. *Organometallics* **1989**, *8*, 2282.

[5] Bernasconi, C. F.; Flores, F. X.; Sun, W. *J. Am. Chem. Soc.* **1995**, *117*, 4875.

[6] A double-mixing stopped-flow apparatus allows the quenching of the anion with acid a few milliseconds after it has been formed by the reaction of the carbene complex with base, i.e., before it starts to decompose.

[7] Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **1993**, *115*, 12526.

[8] Bernasconi, C. F.; Sun, W. *Organometallics* **1997**, *16*, 1926.

[9] Bernasconi, C. F.; Leyes, A. E. *J. Am. Chem. Soc.* **1997**, *119*, 5169.

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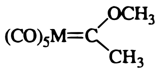
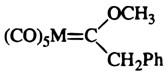
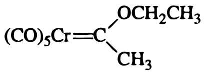
determined in 50% acetonitrile−50% water (v/v) and in pure water (**1-Cr** only).[4]



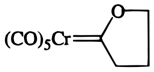
1-Mo (M = Mo)
1-W (M = W)



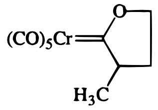
2-Cr (M = Cr)
2-W (M = W)



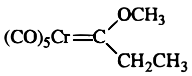
3-Cr



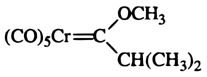
4-Cr



5-Cr



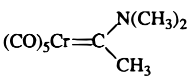
6-Cr



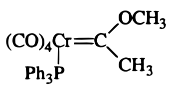
7-Cr

Thermodynamic acidities are very useful in evaluating electronic effects on Fischer carbene complexes and their respective anions. For example, comparison of the pK_a^{CH} values of **1-Cr**, **1-Mo**, and **1-W** revealed that the stability of **1-M**$^-$ depends little on the metal;[8] comparison of the pK_a^{CH} values of **1-Cr**, **6-Cr**, and **7-Cr** indicated that methyl groups on the α-carbon stabilize the anion,[11] consistent with the notion that the resonance structure of **1-Cr**$^-$ with the C═C double bond is dominant;[10] comparison of the pK_a^{CH} values of **1-Cr** and **4-Cr** shows **4-Cr** to be much less acidic, presumably because π-donation by the oxygen in the neutral carbene complex is more effective in stabilizing **4-Cr** than **1-Cr**, due to the ring structure which locks the oxygen into a position for better π-overlap.[9]

A drawback of water or aqueous acetonitrile as the medium for acidity determinations is that the range of pK_a^{CH} values accessible to measurement is relatively narrow and does not allow the study of the acidity of more weakly acidic carbene complexes than **4-Cr** ($pK_a^{CH} = 14.47$ in 50% acetonitrile−50% water). It would therefore be desirable to establish an acidity scale of carbene complexes in a common solvent suitable for a large variety of such complexes, including very weakly acidic ones, e.g., amino carbene complexes such as **8-Cr** or complexes where one of the CO ligands is replaced by less electron withdrawing ones, e.g., **9-Cr**. Such pK_a^{CH} measurements are not only of theoretical interest but highly relevant to the synthetic chemist who uses carbanions derived from such carbene complexes as nucleophiles.[12]



8-Cr



9-Cr

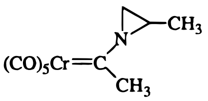
THF, a solvent commonly used in synthetic applications, would certainly allow ionization of even the least acidic carbene complexes but ion-pairing effects are so severe in this medium that quantitative measurements are strongly affected or distorted. For example, the apparent acidity of **1-Cr** in THF as measured by the equilibrium constant of the reaction of **1-Cr** with the PPN$^+$ [15] salt of *p*-cyanophenoxide ion[3] is 10^4 fold higher than that obtained for the reaction of **1-Cr** with lithium methoxide,[16] presumably the consequence of differences in the tightness of the ion pairs in the two systems. We shall return to this point in the Discussion.

DMSO, a standard solvent for acidity determinations pioneered by Bordwell,[17] tends to oxidize Fischer carbene complexes quite rapidly,[18] although for **8-Cr** this decomposition was slow enough to allow a pK_a^{CH} determination.[13]

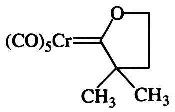
Pure acetonitrile, which, for example, has been successfully used for acidity measurements of hydrido transition metal complexes[19] and transition metal acyl compounds,[20] appears to be the best candidate. Fischer carbene complexes are quite stable in this solvent; its polarity is high enough that ion pairing should not be a significant problem and pK_a values up to about 36 can be measured.[21] In this paper we present the results of pK_a^{CH} measurements of a series of Fischer carbene complexes in this solvent.

Experimental Section

Substrates. All carbene complexes used in this work except for **5-Cr**, **10-Cr**, and **11-Cr** were available from previous studies.[1,7−10,13,24−26]



10-Cr



11-Cr

Preparation of Pentacarbonyl(5-methyl-2-oxacyclopentylidene)chromium(0), 5-Cr. A solution of pentacarbonyl(2-oxacyclopentylidene)chromium(0)[23] (2.590 g) in 200 mL of ether was cooled to −78 °C under argon atmosphere and 1 equiv of *n*-BuLi was added. After 15 min at −78 °C, the anion was transferred via cannula to a solution of MeOTf (5 equiv) in 20 mL of ether at 0 °C over 75 min. The reaction mixture was stirred at 0 °C for another 10 min before being quenched by adding saturated aqueous $NaHCO_3$ solution (100 mL). The organic layer was washed with another 100 mL of $NaHCO_3$ solution and 100 mL of brine and then dried over $MgSO_4$. Flash column chromatography provided a yellow oil (1.78 g, 65%, $R_f = 0.27$, 10% CH_2Cl_2 in hexane). The ratio of the mono- and dialkylation products was determined by ^1H NMR.[23]

Preparation of Pentacarbonyl(5,5-dimethyl-2-oxacyclopentylidene)chromium(0), 11-Cr. The above procedure was followed on a 400-mg scale to provide a mixture of non-, mono-, and dimethylated pentacarbonyl(2-oxacyclopentylidene)chromium(0) derivatives (77% yield, non-:mono-:di- = 1:4:1). The mixture (368.8 mg) was dissolved

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[10] Bernasconi, C. F.; Sun, W.; García-Río, L.; Kittredge, K. *J. Am. Chem. Soc.* **1997**, *119*, 5583.

[11] Based on statistically corrected pK_a^{CH} values which follow the order pK_a^{CH}(**1-Cr**) > pK_a^{CH}(**6-Cr**) > pK_a^{CH}(**7-Cr**).[10]

[12] This aspect has been extensively discussed by Wulff et al.[13,14]

[13] Wulff, W. D.; Anderson, B. A.; Toole, A. J.; Xu, Y.-C. *Inorg. Chim. Acta* **1994**, *220*, 215.

[14] Shi, Y.; Wulff, W. D.; Yap, G. P. A.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1996**, 2601.

[15] PPN$^+$ = bis(triphenylphospine)iminium ion.

[16] Anderson, R. L. Ph.D. Thesis, University of Wisconsin, 1974.

[17] Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

[18] (a) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (b) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726.

[19] (a) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (b) Kristjansdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; Verlag Chemie: New York, 1992; p 309.

[20] Fermin, M. C.; Thiyagarajan, B.; Bruno, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 974.

[21] The ionic product of acetonitrile is approximately 10^{-44} but in the presence of stronger bases rapid self-condensation of the solvent starts to interfere.[22a]

[22] (a) Schwesinger, R.; Schlemper, H. *Angew Chem., Int. Ed. Engl.* **1987**, *26*, 1167. (b) Schwesinger, R. *Chimia* **1985**, *39*, 269.

[23] Casey, C. P.; Anderson, R. L. *J. Organomet. Chem.* **1974**, *73*, C28.

[24] Xu, Y.-C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263.

[25] Powers, T. S.; Shi, Y.; Wilson, K. J.; Wulff, W. D. *J. Org. Chem.* **1994**, *59*, 6882.

[26] Rahm, A.; Wulff, W. D.; Rheingold, A. L. *Organometallics* **1993**, *12*, 597.

in 10 mL of ether at −60 °C under argon followed by the addition of 1 equiv of *n*-BuLi. After 30 min at −60 °C, 1 equiv of MeOTf was added, and the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was recooled to −60 °C and another 0.2 equiv of *n*-BuLi was added. After 1 h at −60 °C, the reaction mixture was transferred via cannula to a solution of MeOTf (0.4 equiv) in 5 mL of ether at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and another 1.5 h at room temperature before being quenched by adding saturated aqueous $NaHCO_3$ solution (30 mL). The yellow organic layer was washed with another 20 mL of $NaHCO_3$ solution and 20 mL of brine and then dried over $MgSO_4$. Flash column chromatography provided a yellow solid (239.7 mg, 62%, $R_f = 0.18$, hexane). ^1H NMR ($CDCl_3$) δ1.42 (s, 6H), 1.80 (t, 2H, $J = 7.3$ Hz), 4.86 (t, 2H, $J = 7.3$ Hz).

Preparation of Pentacarbonyl[(2-methylaziridinyl)(methyl)carbene]chromium(0), 10-Cr. The procedure described by Rudler et al. was used.[27] Following column chromatography on silica gel (100−200 mesh, eluent ethyl ether−CH_2Cl_2 80:20) and evaporation of the solvent a pale yellow oil was obtained which appears to be a mixture of *E* and *Z* isomers. ^1H NMR ($CDCl_3$) δ1.49 and 1.67 (d, CH_3), 2.70 (m, CH and CH_2), 3.11 and 3.38 (s, CH_3). ^{13}C NMR ($CDCl_3$) δ_C 15.1 and 16.8 (ring CH_3), 31.6 and 32.5 (CH_3), 35.2 and 36.4 (CH), 39.8 and 40.9 (CH_2), 217.9 (CO), 223.2 (CO), 266.7 and 268.4 (C=).

Other Materials. 1,1,2,2-Tetramethylguanidine (TMG) from Aldrich was dried overnight over barium oxide and fractionally distilled under argon. The amines 2-(*tert*-butylimino)-2-(diethylamino)-1,3-dimethylperhydro-1,3-diazaphosphorine (BEMP) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) were purchased from Fluka and used as received. All operations were conducted under argon and transfers of liquid reagents from their storage containers to the reaction vessels were done following standard septum/syringe techniques. Acetic acid was purchased from Fischer Scientific and used in pH-jump experiments without further purification.

Acetonitrile was available from three sources and was treated as described below:

(a) Aldrich, A.C.S. grade acetonitrile was dried following a literature procedure.[28] After predrying it over 3 Å molecular sieves it was distilled from P_4O_{10} under argon and then distilled from CaH_2, and the middle fraction was collected. The dry solvent was then degassed by several freeze−pump−thaw cycles and stored in a tightly closed container under argon.

(b) Dry PerSeptive Biosystems acetonitrile[29] was used as received and kept in the original container provided with a rubber septum. Transfers were done by syringe to avoid exposure to air and moisture.

(c) Fischer Optima acetonitrile was allowed to stand over P_4O_{10} overnight and then distilled under argon, discarding the first 50 mL. The suggestion by Burfield et al.[30] of static drying was followed, as opposed to drying with stirring. The dry solvent was then degassed by several freeze−pump−thaw cycles and stored in a tightly closed container under argon.

Experiments were run in all three solvents with identical results. Fischer's Optima acetonitrile was adopted as our standard solvent. All syringes, flasks, and spectrophotometric cells used in these experiments were dried overnight in a desiccator with $CaSO_4$ in vacuo. Syringes and pipets were rinsed with the dry solvent/solution at least twice before the final transfer.

Methodology. Equilibrium constants for the reaction of the carbene complexes with amines such as TMG, DBU, and BEMP were measured spectrophotometrically by exploiting the large differences between the extinction coefficients of the carbene complex (CH) and its anion (C^-) at chosen wavelengths. In most cases, ratios, *r*, were determined via eq 4 where [CH] and $[CH]_o$ refer to the concentration of CH in the

$$r = \frac{[CH]}{[CH]_o} = \frac{A - A_\infty}{A_o - A_\infty} \qquad (4)$$

presence and absence of amine, respectively, *A* is the absorbance at intermediate amine concentrations (partial conversion of CH into C^-), A_∞ the absorbance at high amine concentrations (complete conversion to C^-) and A_o the absorbance in the absence of amine. In some cases where the extinction coefficients of CH and C^- were accurately determined (**1-Cr** and **4-Cr**) the relationship between [CH] and $[CH]_o$ shown in eq 5 was applied to the calculation of [CH], with equal results.

$$[CH] = \frac{A - \epsilon_C[CH]_o}{\epsilon_{CH} - \epsilon_C} \qquad (5)$$

The concentrations of the other species involved in the acid−base equilibria were found using the appropriate expressions, eq 6−8, based

$$[CH] = r[CH]_o \qquad (6)$$

$$[C^-] = (1 - r)[CH]_o = [BH^+] \qquad (7)$$

$$[B] = [B]_o - [BH^+] \qquad (8)$$

on a model that assumes dissociation into free ions, eqs 9 and 10.

$$CH + B \overset{K_1}{\rightleftharpoons} C^- + BH^+ \qquad (9)$$

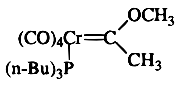
$$K_1 = \frac{[C^-][BH^+]}{[CH][B]} \qquad (10)$$

In the case of **5-Cr** some corrections to the measured absorbance values had to be applied in order to account for the fact that the sample contained 12% of the dimethyl derivative **11-Cr**. It was assumed that **11-Cr** does not undergo any reaction with the base but simply provides some background absorption to the spectra of the reaction solutions. This background absorption was calculated on the basis of the measured extinction coefficients of **11-Cr** ($\epsilon_{350} = 5750$ M^{-1} cm^{-1} and $\epsilon_{370} = 7800$ M^{-1} cm^{-1}) and subtracted from the measured A_o, *A*, and A_∞ values before eq 4 was applied.

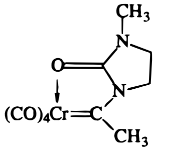
Instrumentation. All UV measurements were made in a thermostated Hewlett-Packard 8245A spectrophotometer. The ^1H NMR spectra were taken in a General Electric 500 MHz spectrometer.

Results

General Features. The determination of ionization constants was attempted for **1-Cr**, **3-Cr**, **4-Cr**, **5-Cr**, **6-Cr**, **7-Cr**, **8-Cr**, **9-Cr**, **10-Cr**, **12-Cr**, **13-Cr**, **14-Cr** and **15-Cr**. The bases used were 1,1,2,2-tetramethylguanidine (TMG), 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), and 2-(*tert*-butylimino)-2-(diethylamino)-1,3-dimethylperhydro-1,3-diazaphosphorine (BEMP)



12-Cr



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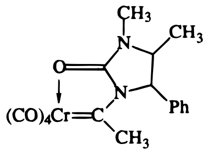

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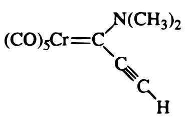

15-Cr

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[27] (a) Denise, B.; Parlier, A.; Rudler, H.; Vaissermann, J.; Daran, J. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1303. (b) Denise, B.; Parlier, A.; Rudler, H.; Vaissermann, J. *J. Organomet. Chem.* **1995**, *494*, 43.

[28] Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

[29] Certified water content ≤ 9 ppm.

[30] Burfield, D. R.; Lee, K.-H.; Smithers, R. H. *J. Org. Chem.* **1977**, *18*, 3060.

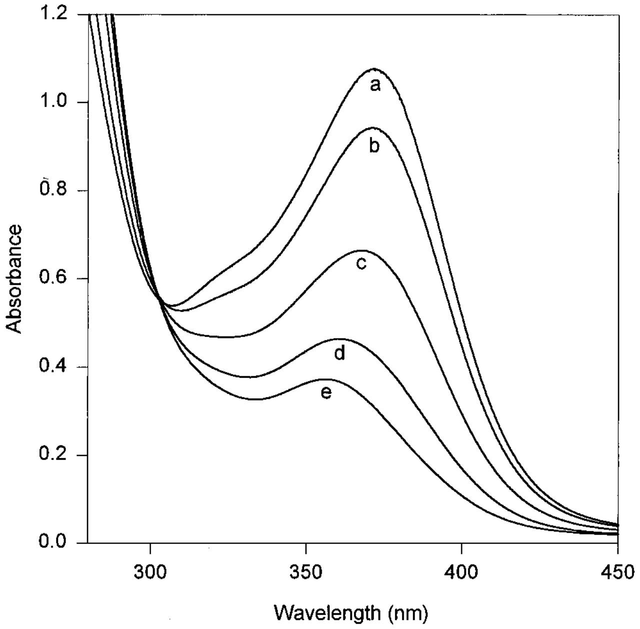

Figure 1. Spectra of **1-Cr** (1.31×10^{-4} M) in the presence of increasing amounts of TMG. a: no TMG added, (b) $[\mathrm{TMG}]_o = 2.6 \times 10^{-5}$ M; c: $[\mathrm{TMG}]_o = 7.8 \times 10^{-5}$ M; d: $[\mathrm{TMG}]_o = 1.30 \times 10^{-4}$ M; e: $[\mathrm{TMG}]_o = 2.08 \times 10^{-4}$ M.

whose $\mathrm{p}K_\mathrm{a}^\mathrm{BH}$ values in acetonitrile are 23.3,[31] 24.32,[22b] and 27.58,[22b] respectively.

In a typical experiment, a solution containing the carbene complex was mixed with a base solution; in most cases the ionization equilibrium was established within a few seconds or less as seen by taking absorption spectra as a function of time. As previously described for aqueous acetonitrile solutions,[7,9] the anions of chromium carbene complexes are characterized by a significantly reduced absorbance in the 330−420 nm region and a slight hypsochromic shift of $\lambda_{\max}$ in that region. A representative set of spectra is shown in Figure 1 for the reaction of **1-Cr** with TMG.

Even though there can be no doubt that the observed equilibria indeed represent proton transfer, confirmation comes from ^{1}H NMR spectra of reaction solutions of **1-Cr** in the presence of TMG. **1-Cr** was chosen for this experiment because it is the most acidic of our carbene complexes and requires the least amount of TMG to achieve deprotonation. Hence the NMR spectrum does not become overwhelmed by the TMG signals. In a solution of 0.06 M **1-Cr** and 0.088 M TMG which leads to approximately 95% ionization, the methyl signal at δ 2.98 ppm is no longer detectable while two new singlets appear at δ 3.82 and 4.62 ppm. In accordance with findings reported by Casey and Anderson,[3] the new signals must refer to the nonequivalent (diastereotopic) vinyl hydrogens in **1-Cr**$^-$; for the PPN$^+$ salt[15] of **1-Cr**$^-$ in THF, these signals appear at δ 3.78 and 4.52 ppm, respectively.[3]

In most cases the absorption spectrum of the equilibrium mixture in the presence of base was stable for several minutes. Reversibility of the ionization was tested by adding small amounts of acetic acid to the solution and comparing the UV spectrum of the recovered carbene complex with that of the original sample. Typically, recovery of the carbene complex amounted to approximately 90% if the acid quench occurred immediately after the ionization equilibrium was established, but to progressively less than 90% if the quench was delayed. This indicates gradual decomposition of the anion; this decomposition was not further investigated but it is likely that it represents reaction of the anion (C$^-$) with the protonated base which leads to the corresponding vinyl ether, as described by Fischer et al.[32] and Casey et al.[33]

Not all attempts at measuring ionization constants were successful, either because decomposition of the anion became extensive before the ionization equilibrium was fully established (**7-Cr**, **13-Cr**, **14-Cr**, and **15-Cr**) or because the acidity of the carbene complex was too low to lead to measurable ionization even with the strongest base (**8-Cr**).

We now describe the results in some detail.

1-Cr, 3-Cr, 4-Cr, and 5-Cr. Experiments were performed with TMG. Deprotonation of the carbene complex occurred rapidly, and the absorbance of the equilibrated solutions was quite stable over several minutes. The results at various initial concentrations of CH and B are reported in Table 1 for a representative example (**4-Cr**); the results for **1-Cr**, **3-Cr** and **5-Cr** are summarized in Tables S1−S3 of the Supporting Information.[34] Average $\mathrm{p}K_\mathrm{a}^\mathrm{CH}$ values are reported in Table 2.

6-Cr. Experiments were performed with TMG, with A_∞ (eq 4) determined either in the presence of TMG or DBU, with identical results. Deprotonation of **6-Cr** was relatively slow and, depending on the base concentration, it took up to 30 s or longer to reach equilibrium. As a result, decomposition of the anion became significant before the ionization equilibrium was fully established. A correction was therefore applied by linearly extrapolating the absorbance values to "zero time". This correction procedure was quite adequate for experiments at relatively high base concentrations which lead to small *r* ratios. At low base concentrations the rate of deprotonation was too slow relative to the rate of decomposition to yield reliable and reproducible results even after correction. Hence we only report data up to $r = 0.56$ (Table S4).[34]

7-Cr. With this compound, deprotonation by TMG was even slower than with **6-Cr** and of comparable rate with the decomposition of the anion. Hence no meaningful results could be obtained.

8-Cr. This carbene complex is not acidic enough to undergo measurable deprotonation by any of the bases. For example, even a 0.028 M solution of BEMP is unable to significantly deprotonate a 1.50×10^{-4} M solution of **8-Cr**. If under these conditions 5% of the carbene complex were deprotonated, a lower limit for the $\mathrm{p}K_\mathrm{a}^\mathrm{CH}$ of **8-Cr** could be calculated as 32.5.

9-Cr and 12-Cr. These two carbene complexes are significantly less acidic than **1-Cr**, **3-Cr**, **4-Cr**, **5-Cr,** and **6-Cr** but could still be deprotonated in the presence of relatively large concentrations of TMG. A_∞ values in the presence of TMG, DBU, or BEMP were all indistinguishable. As was the case for **6-Cr**, deprotonation was relatively slow which required extrapolation to "zero time" to correct for the onset of decomposition. The results are summarized in Tables S5 and S6.[34]

10-Cr. With this complex, no ionization was observed with either TMG or DBU but in the presence of BEMP deprotonation did occur. However, the rate was quite slow, again necessitating extrapolation to "zero time" as described for **6-Cr**. The results are reported in Table S7.[34]

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[31] Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23.

[32] Fischer, E. O.; Maasböl, A. *J. Organomet. Chem.* **1968**, *12*, P15. (b) Fischer, E. O.; Plabst, W. *Chem. Ber.* **1974**, *107*, 3326.

[33] Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895.

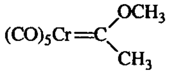
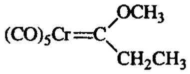
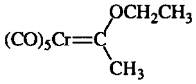
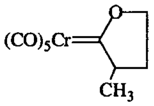
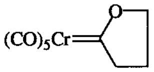
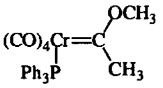
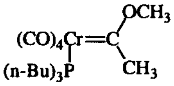
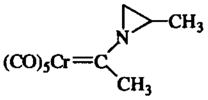
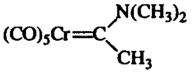
[34] See paragraph concerning Supporting Information at the end of this paper.

Table 1. Experimental Data for the Ionization of **4-Cr** in the Presence of TMG in Acetonitrile at 25 °C[a]

$[CH]_o$,[b] M	$[B]_o$,[b] M	*r*	[CH],[c] M	[B],[c] M	$[C^-]$,[c] M	$[BH^+]$,[c] M	K_1[d]	pK_a^{CH} [e]
8.68×10^{-5}	1.60×10^{-4}	0.72	6.25×10^{-5}	1.36×10^{-4}	2.43×10^{-5}	2.43×10^{-5}	6.97×10^{-2}	24.46
8.68×10^{-5}	2.42×10^{-4}	0.64	5.56×10^{-5}	2.11×10^{-4}	3.12×10^{-5}	3.12×10^{-5}	8.34×10^{-2}	24.38
1.27×10^{-4}	4.03×10^{-4}	0.61	7.75×10^{-5}	3.53×10^{-4}	4.95×10^{-5}	4.95×10^{-5}	8.96×10^{-2}	24.35
8.51×10^{-5}	5.64×10^{-4}	0.52	4.43×10^{-5}	5.23×10^{-4}	4.08×10^{-5}	4.08×10^{-5}	7.21×10^{-2}	24.44
2.92×10^{-5}	2.01×10^{-4}	0.51	1.49×10^{-5}	1.87×10^{-4}	1.43×10^{-5}	1.43×10^{-5}	7.36×10^{-2}	24.43
5.83×10^{-5}	4.03×10^{-4}	0.46	2.68×10^{-5}	3.72×10^{-4}	3.15×10^{-5}	3.15×10^{-5}	9.95×10^{-2}	24.30
1.16×10^{-4}	1.21×10^{-3}	0.44	5.10×10^{-5}	1.15×10^{-3}	6.50×10^{-5}	6.50×10^{-5}	7.22×10^{-2}	24.44
2.93×10^{-5}	4.03×10^{-4}	0.36	1.05×10^{-5}	3.84×10^{-4}	1.88×10^{-5}	1.88×10^{-5}	8.68×10^{-2}	24.36
2.93×10^{-5}	8.06×10^{-4}	0.27	7.91×10^{-6}	7.85×10^{-4}	2.14×10^{-5}	2.14×10^{-5}	7.37×10^{-2}	24.43
1.14×10^{-4}	3.22×10^{-3}	0.21	2.39×10^{-5}	3.13×10^{-3}	9.01×10^{-5}	9.01×10^{-5}	1.08×10^{-1}	24.27

[a] Values of *r* are averages of determinations at 350 and 364 nm. [b] Total concentrations. [c] Equilibrium concentrations. [d] From eq 10. [e] $pK_a^{CH} = pK_a^{BH} - \log K_1$.

Table 2. Summary of K_1 and pK_a^{CH} Values at 25 °C

Carbene Complex		K_1 [a]	pK_a^{CH} (MeCN)	pK_a^{CH}(corr)[b] (MeCN)	pK_a^{CH}(corr)[b] (50% MeCN)[c]	$^{50}\Delta^{A}pK_a$ [d]
	**(1-Cr)**	11.8 ± 5.3	22.2 ± 0.2	22.7 ± 0.2	12.98 [g]	9.7
	**(6-Cr)**	2.62 ± 0.57	22.9 ± 0.1	23.2 ± 0.1	12.62 [h]	10.6
	**(3-Cr)**	1.13 ± 0.63	23.2 ± 0.3	23.7 ± 0.3	13.46 [i]	10.2
	**(5-Cr)**	0.369 ± 0.140	23.7 ± 0.2	24.2 ± 0.2	13.4 [j]	10.5
	**(4-Cr)**	(8.29 ± 1.31) × 10^{-2}	24.4 ± 0.1	24.7 ± 0.1	14.77 [k]	9.9
	**(9-Cr)**	(7.82 ± 1.30) × 10^{-3}	25.4 ± 0.1	25.9 ± 0.1		
	**(12-Cr)**	(6.44 ± 1.21) × 10^{-4}	26.5 ± 0.1	27.0 ± 0.1		
	**10-Cr**	0.95 ± 0.45[e]	27.6 ± 0.2	28.1 ± 0.2		
	**(8-Cr)**	f	≥ 32.5	≥33.0		

[a] Reaction with B = TMG; $pK_a^{BH} = 23.3$. [b] Statistically corrected for the number of equivalent protons. [c] pK_a^{CH} in 50% MeCN−50% water at 25 °C. [d] $^{50}\Delta^{A}pK_a^{CH} = pK_a^{CH}(\mathrm{MeCN}) - pK_a(50\%\ \mathrm{MeCN})$. [e] Reaction with B = BEMP; $pK_a^{BH} = 27.58$. [f] No detectable ionization with BEMP, see text. [g] Reference 7. [h] Reference 10. [i] Reference 8. [j] Reference 1. [k] Reference 9.

13-Cr and 14-Cr. No meaningful data could be obtained with these compounds in the presence of any of the bases. With TMG, deprotonation is quite slow and decomposition of the anion too fast to allow extrapolations of absorbance values as was done for **6-Cr**, **9-Cr**, **10-Cr**, and **12-Cr**. With BEMP a fast initial spectral change was observed; however, a quench with acetic acid did not regenerate the carbene complexes.

15-Cr. No reaction was observed with TMG. With DBU and BEMP ionization appears to occur but attempts at regenerating the starting material after adding acetic acid failed, suggesting very rapid decomposition of the anion. Again, no meaningful quantitative data can be reported on this compound.

Discussion

Reliability of the Results. As described in the Results section, in most cases reaction of the carbene complexes with the base (mainly TMG) is clean, as demonstrated by sharp isosbestic points, and leads to equilibrium mixtures that are stable enough for precise absorbance measurements. In some cases (**6-Cr**, **9-Cr**, **10-Cr**, **12-Cr**), minor corrections to the absorbance values had to be applied to take into consideration the onset of decomposition. In the case of **1-Cr**, ^{1}H NMR spectra in the presence of TMG also confirmed that the reaction indeed represents deprotonation. Reversibility of the deprotonation was demonstrated by regenerating the carbene complex upon addition of acetic acid to solutions of the anion. Typically, around 90% recovery was observed although with **10-Cr** only about 80% of the starting material could be regenerated; in no case did the recovery approach 100%, implying that even in the most favorable cases some decomposition of the anion could not be avoided. This feature is unlikely to grossly distort the calculated equilibrium constants but some systematic error beyond the standard deviations shown in Table 2 may affect the reported pK_a^{CH} values because of this decomposition.

Ionization Model. The initial concentrations of the carbene complex and the base were chosen such that the resulting r ratios would fall between about 0.15 to 0.20 and 0.80 to 0.85. For r values outside this range the calculated equilibrium concentrations become very sensitive to experimental error, potentially giving misleading results. As long as r was kept within this range, the K_1 values determined based on the free ion model of eqs 9 and 10 deviated randomly from their average. This lack of trend in K_1 supports the assumption that C^- and BH^+ are formed mainly as free ions. This result is also consistent with other acid−base equilibrium studies of transition metal compounds such as hydrido transition metal complexes[19] and transition metal acyl compounds.[20] Furthermore, it indicates that homo-hydrogen-bonding complexation between TMG and TMGH$^+$ is insignificant or absent; in fact the homoconjugation association constant between TMG and TMGH$^+$ has recently been shown to be 1.9 M^{-1},[35] which is much too small to affect our results.

Even though, as stated above, our results are consistent with the free ion model of eq 9, the question whether ion pairing might be significant, e.g., eq 11, needs to be addressed. In a

$$\mathrm{CH} + \mathrm{B} \overset{K_i}{\rightleftharpoons} \mathrm{C^-{\cdot}BH^+} \overset{K_d}{\rightleftharpoons} \mathrm{C^-} + \mathrm{BH^+} \qquad (11)$$

series of papers dealing with the ionization of various carbon acids by amine bases, spectrophotometric equilibrium measurements appeared to be consistent mainly with ion-pair formation (small or zero K_d in eq 11).[36] However, on the basis of conductivity measurements, Galezowski and Jarczewski[37] could show that the spectrophotometric results were misleading and that in most cases C^- and BH^+ exist as free ions rather than ion pairs (large K_d), particularly with B = TMG and DBU.

The possible presence of small amounts of ion pairs with some Fischer carbene complexes, especially **1-Cr**, suggests itself by a nonnegligible trend toward lower K_1 (higher pK_a^{CH}) with increasing r (smaller degrees of ionization) as seen in Table S1.[34] A treatment of the results in terms of eq 11 actually provides a reasonably good fit with the data. The equations necessary for the fit to eq 11 are described in an appendix included under Supporting Information[34] and the results of the fit are reported in Table S8.[34] This treatment yields $K_i = (7.12 \pm 0.18) \times 10^4$ M^{-1} and $K_d = (7 \pm 4) \times 10^{-6}$ M. Although less pronounced than for **1-Cr**, the data for **3-Cr** suggest that there also may be a trend toward lower K_1 with increasing r and hence we have applied the model of eq 11 to this carbene complex as well (Table S9);[34] it affords $K_i = (1.38 \pm 0.06) \times 10^4$ M^{-1} and $K_d = (4 \pm 2) \times 10^{-6}$ M.

Whether **1-Cr** and possibly **3-Cr** truly lead to ion-pair formation whereas the other carbene complexes do not is unclear at this point. A possible reason only **1-Cr** and **3-Cr** would be more prone to ion-pair formation than the other carbene complexes is that **1-Cr** and **3-Cr** are less bulky around the centers of negative charge in the anion (α-carbon and chromium moiety), thus leading to less steric repulsion between the ions. Be it as it may, in the following discussion we shall assume that the pK_a^{CH} values obtained for **1-Cr** and **3-Cr** based on the free ion model are valid. This assumption is supported by the fact that the trends seen in these pK_a^{CH} values are consistent with the results in aqueous acetonitrile.

Solvent Effect on pK_a^{CH}. The pK_a^{CH} values determined in this study are summarized in Table 2. The table includes pK_a^{CH} values in 50% *aqueous* acetonitrile which are available for five of the carbene complexes. The pK_a^{CH} values in acetonitrile are, on average, about 10.2 units higher than in 50% aqueous acetonitrile. This difference in pK_a^{CH} may be expressed by eq 12 where ${}^{50}\gamma_{C^-}^{A}$, ${}^{50}\gamma_{H^+}^{A}$, and ${}^{50}\gamma_{CH}^{A}$ are the solvent

$$ {}^{50}\Delta^{A}pK_a^{CH} = pK_a^{CH}(\mathrm{MeCN}) - pK_a^{CH}(50\%\ \mathrm{MeCN}) = \log {}^{50}\gamma_{C^-}^{A} + \log {}^{50}\gamma_{H^+}^{A} - \log {}^{50}\gamma_{CH}^{A} \qquad (12)$$

activity coefficients for the transfer of C^-, H^+, and CH, respectively, from 50% MeCN−50% water ("50") to pure MeCN ("A").[38] The largest contribution to ${}^{50}\Delta^{A}pK_a^{CH}$ must come from the $\log {}^{50}\gamma_{C^-}^{A}$ term: for the transfer of H^+ from pure water (W) to acetonitrile, $\log {}^{W}\gamma_{H^+}^{A} = 8.1$,[39] reflecting the much weaker solvation of H^+ in acetonitrile. The value for $\log {}^{50}\gamma_{H^+}^{A}$ is not known but it is probably not substantially lower than 8.1. This leaves a contribution of perhaps 2.5 to 3.0 log units of ${}^{50}\Delta^{A}pK_a^{CH}$ to be accounted for by $\log {}^{50}\gamma_{C^-}^{A} - \log {}^{50}\gamma_{CH}^{A}$, which probably results from a combination of weaker solvation of C^- ($\log {}^{50}\gamma_{C^-}^{A} > 0$) and stronger solvation of CH ($\log {}^{50}\gamma_{CH}^{A} < 0$) in pure acetonitrile.

In the case of **1-Cr** the pK_a^{CH} has also been determined in 5% MeCN−95% water;[7] its value in this solvent is 12.77[7] or $pK_a^{CH}(\mathrm{corr}) = 13.25$ which leads to ${}^{5}\Delta^{A}pK_a = 9.4$.[41] If one assumes ${}^{5}\log_{H^+}^{A} \approx \log {}^{W}\gamma_{H^+}^{A} = 8.1$ this leaves a contribution by $\log {}^{5}\gamma_{C^-}^{A} - \log {}^{50}\gamma_{CH}^{A}$ to ${}^{5}\Delta^{A}pK_a^{CH}$ of only 1.3.

Relative Acidities. On the basis of statistically corrected pK_a^{CH} values the relative acidity order in acetonitrile is **1-Cr** > **6-Cr** > **3-Cr** ≈ **5-Cr** > **4-Cr** > **9-Cr** > **12-Cr** > **10-Cr** ≫ **8-Cr**. For those carbene complexes whose pK_a^{CH} values are known in 50% MeCN−50% water the order in the latter solvent is **6-Cr** > **1-Cr** > **5-Cr** > **3-Cr** > **4-Cr**, which is not quite the same as in pure acetonitrile. The change is mainly the result of a stronger reduction in acidity of **6-Cr** and **5-Cr** upon transfer from aqueous to pure acetonitrile (larger ${}^{50}\Delta^{A}pK_a^{CH}$ values). A

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(35) Galezowski, W.; Jarczewski, A.; Stanczyk, M.; Brzezinski, B.; Bartl, F.; Zundel, G. *J. Chem. Soc., Faraday Trans.*, submitted, cited in Galezowski, W.; Stanczyk, M.; Jarczewski, A. *Can. J. Chem.* **1997**, *75*, 285.

(36) Numerous citations can be found in ref 37.

(37) (a) Galezowski, W.; Jarczewski, A. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1647. (b) Galezowski, W.; Jarczewski, A. *Can J. Chem.* **1992**, *70*, 935.

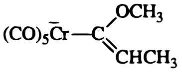
(38) $\log {}^{I}\gamma_{X}^{II}$ for the transfer of X from solvent I to solvent II is given by ${}^{I}\Delta^{II}G_{tr}^{o}(X)/2.3RT$ with ${}^{I}\Delta^{II}G_{tr}^{o}(X)$ being the standard free energy of transfer, Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.

(39) Based on ${}^{W}\Delta^{A}G_{tr}(H^+) = 11.0$.[40.]

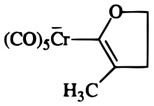
(40) Kolthoff, I. M.; Chantooni, M. K. *Anal. Chem.* **1972**, *44*, 194; *J. Phys. Chem.* **1972**, *76*, 2026.

(41) There is also a pK_a^{CH} of **1-Cr** in pure water ($pK_a^{CH} = 12.3$)[4] but this value is at 20 °C.

possible interpretation of these findings is as follows. The fact that in aqueous acetonitrile **6-Cr** is more acidic than **1-Cr** and **5-Cr** is more acidic than **4-Cr** has been attributed to the extra methyl group which stabilizes the corresponding anions (**6-Cr**$^-$ and **5-Cr**$^-$) relative to **1-Cr**$^-$ and **4-Cr**$^-$, respectively.[1,9]

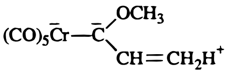

$(CO)_5\bar{C}r{-}C(OCH_3){=}CHCH_3$

6-Cr$^-$



5-Cr$^-$

Assuming that the dominant resonance structures of the anions have the negative charge mainly delocalized into the $(CO)_5Cr$ moiety, the increased stability of **6-Cr**$^-$ over **1-Cr**$^-$, and of **5-Cr**$^-$ over **4-Cr**$^-$ simply reflects the well-known stabilization of alkenes by methyl or alkyl groups.[42] This stabilization is commonly attributed to hyperconjugation[42] although other factors are believed to contribute as well.[43] The stronger reduction in the acidities of **6-Cr** and **5-Cr** compared to those of the other carbene complexes upon transfer from aqueous to pure acetonitrile may then be the result of a reduction in the hyperconjugative stabilization of **6-Cr**$^-$ and **5-Cr**$^-$, respectively. This is because the hyperconjugative structures, e.g. **6-Cr**$^-$**(h)**, carry multiple charges that are less well supported in the less polar pure acetonitrile. For **5-Cr**, whose pK_a^{CH}(corr) in 50% MeCN$-$50% water is about 1.45 pK_a units lower than for **4-Cr**, the solvent effect is not enough to reverse the relative acidities of **5-Cr** and **4-Cr**, but it reduces the difference in their pK_a^{CH} values from 1.45 to 1.0. On the other hand, for **6-Cr** with a pK_a^{CH}(corr) that in the aqueous acetonitrile is only 0.4 units lower than for **1-Cr**, the solvent effect leads to a reversal of the relative acidities between **1-Cr** and **6-Cr**.

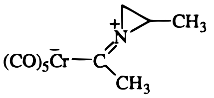

$(CO)_5\bar{C}r{-}\bar{C}(OCH_3){-}CH{=}CH_2H^+$

6-Cr$^-$(h)

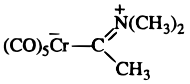
With respect to the relative acidities of **1-Cr**, **3-Cr**, and **4-Cr**, they follow the same order in both solvents, i.e., **1-Cr** > **3-Cr** > **4-Cr**. This order reflects the increasing stabilization of the acid form by the π-donor effect of the alkoxy group.[8,9] This effect is particularly strong in **4-Cr** because the ring structure locks the oxygen into a position for better π-overlap with the carbene carbon, as discussed in more detail elsewhere.[9]

As a result of replacing one of the strongly withdrawing CO ligands with the weakly electron withdrawing phosphine ligands, **9-Cr** and **12-Cr** are 3.2 and 4.3 pK_a units, respectively, less acidic than **1-Cr**. These acidity reductions are substantial but not as large as the corresponding pK_a differences in metal hydrides, which range between 6.2 and 10.5 pK_a units. Representative examples (with MeCN pK_a in parentheses) include $CpW(CO)_3H$ (16.1) vs $CpW(CO)_2(PMe_3)H$ (26.6), $HMn(CO)_5$ (14.2) vs $HMn(CO)_4(PPh_3)$ (20.4), and $HCo(CO)_4$ (8.4) vs $HCo(CO)_3(PPh_3)$ (15.4).[19b] The smaller pK_a differences for the Fischer carbene complexes are probably related to the fact that the negative charge in the anion is not entirely delocalized on the metal moiety (see **1-Cr**$^-$).

Of particular interest is the large difference in acidity between **10-Cr** and **8-Cr**. The much higher pK_a values of amino carbene complexes compared to alkoxy carbene complexes is the result of the much stronger π-donor effect of the amino nitrogen compared to that of an alkoxy oxygen. This translates into a pK_a difference between **8-Cr** and **1-Cr** of more than 10 units. On the other hand, the aziridinyl group is a much poorer π-donor[45] than the Me_2N group because ring strain counteracts sp^2 hybridization of the nitrogen. In other words, in the case at hand, the resonance structure **10-Cr**$^\pm$ is less stable than **8-Cr**$^\pm$. This is seen in a pK_a value for **10-Cr** which is more than 5 units lower than the pK_a of **8-Cr**.



10-Cr$^\pm$


$(CO)_5\bar{C}r{-}C(CH_3){=}\overset{+}{N}(CH_3)_2$

8-Cr$^\pm$

Comparison with Acidities in DMSO and THF. There have been a few reports of acidities of Fischer carbene complexes in THF and one report in DMSO. A major difficulty with THF is that there are no free ions in this solvent which makes it difficult to define a pK_a^{CH} that would be directly comparable to pK_a^{CH} values in polar solvents. Nevertheless, some of these acidity data have recently been summarized in terms of pK_a^{CH} values;[13] they are reported as "pK_a^{CH}" in Table 3. The "pK_a^{CH}" values of 8 for **1-Cr**,[3] **4-Cr**,[47]and **5-Cr**[47] in THF are based on equilibrium measurements of the reaction between the respective carbene complex and the PPN$^{+\ 15}$ salt of p-cyanophenoxide ion; "pK_a^{CH}" = 8 is deduced from the fact that the equilibrium constant for the reaction with the *p*-cyanophenoxide salt is about 1 for all three complexes while the aqueous pK_a of *p*-cyanophenol is 8. The "pK_a^{CH}" value of 12 for **1-Cr** was calculated on the basis of the equilibrium constant of the reaction of **1-Cr** with lithium methoxide and the pK_a of methanol.[16] The "pK_a^{CH}" value for **12-Cr** was derived from measurements of the equilibrium constant of the reaction with lithium *tert*-butoxide and the known pK_a of *tert*-butyl alcohol.[24]

The problem with these "pK_a^{CH}" values is that their absolute values have no well-defined physical meaning, especially those in THF. This is not only because of the ion pairing effects but also because they are not based on pK_a values of the proton acceptors determined in THF but in solvents such as water (*p*-cyanophenoxide ion) or methanol (MeO$^-$). Even the *relative* "pK_a^{CH}" values suffer from gross distortions which render their meaning questionable.

For example, the "pK_a^{CH}" value obtained from **1-Cr** depends strongly on the base system used for the deprotonation, i.e., $PPN^+/4\text{-}CNC_6H_4O^-$ vs Li^+/MeO^-. This must be the result of large differences in the tightness or stability of the reactant and/or product ion pairs. Or, the "pK_a^{CH}" values of **1-Cr**, **4-Cr**, and **5-Cr** are about the same in THF which contrasts with

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(42) (a) McMurry, J. *Organic Chemistry*, 3rd ed.; Brooks/Cole: Belmont, CA, 1992; p 190. (b) Fox, M. A.; Whitesell, J. K. *Organic Chemistry*; Jones and Bartlett: New York, 1994; p 40.

(43) For example, the higher stability of **6-Cr**$^-$ relative to **1-Cr**$^-$ may be explained on the basis of a bond strength argument.[44] $C_{sp^2}$$-$H bonds are stronger than $C_{sp^3}$$-$H bonds and $C_{sp^2}-C_{sp^3}$ bonds are stronger than $C_{sp^3}-C_{sp^3}$ bonds but the increase in bond strength is greater for the change from $C_{sp^3}-C_{sp^3}$ to $C_{sp^2}-C_{sp^3}$ than for the change from $C_{sp^3}$$-$H to $C_{sp^2}$$-$H.[42a, 44] Since conversion of **6-Cr** to **6-Cr**$^-$ entails a change of one $C_{sp^3}-C_{sp^3}$ and one $C_{sp^3}$$-$H bond into one $C_{sp^2}-C_{sp^3}$ and one $C_{sp^2}$$-$H bond, respectively, but the conversion of **1-Cr** to **1-Cr**$^-$ involves only changes of two $C_{sp^3}$$-$H bonds to two $C_{sp^2}$$-$H bonds, the conversion of **6-Cr** to **6-Cr**$^-$ is more favorable.

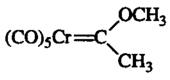
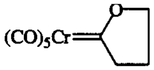
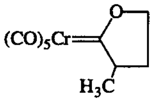
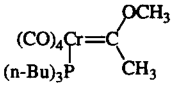
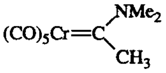
(44) Streitwieser, A.; Heathcock, C. H.; Kosower, E. M. *Introduction to Organic Chemistry*, 4th ed.; Macmillan: New York, 1992; p 258.

(45) The σ_R substituent constants for NMe_2 and 1-aziridinyl are -0.56 and -0.26, respectively.[46]

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

(47) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1976**, *118*, 309.

Table 3. pK_a^{CH} Values of Fischer Carbene Complexes in THF and DMSO

Carbene Complex	Solvent	"pK_a^{CH}"
 **(1-Cr)**	THF	12 (Li^+ MeO^-)[a] 8 (PPN^+ 4-$CN_6H_4O^-$)[b]
 **(4-Cr)**	THF	8 (PPN^+ 4-$CNC_6H_4O^-$)[c]
 **(5-Cr)**	THF	8 (PPN^+ 4-$CNC_6H_4O^-$)[c]
 **(12-Cr)**	THF	18.8 (Li^+ t-BuO^-)[d]
 **(8-Cr)**	DMSO	20.4 (K^+ 2-naphthylacetonitrile anion)[e]

[a] Reference 16. [b] Reference 3. [c] Reference 47. [d] Reference 24. [e] Reference 13.

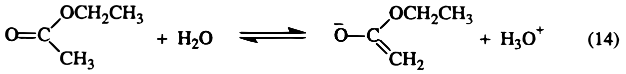
our results in acetonitrile where the measured pK_a^{CH} of **4-Cr** is approximately 2.2 pK_a units and the pK_a^{CH} of **5-Cr** approximately 1.5 units higher than that of **1-Cr**.

With regard to the "pK_a^{CH}" of **8-Cr** in DMSO (20.4), it is 12.1 pK_a units lower than the lower limit estimated in acetonitrile. This is a reasonable result. Carbon acids such as 3-$NO_2C_6H_4CH_2NO_2$, 4-$NO_2C_6H_4CH_2NO_2$, and 3,5-$(NO_2)_2C_6H_3$-CH_2NO_2 have $^{D}\Delta^{A}pK_a^{CH}$ [48] values of 11.7, 12.0, and 11.2, respectively.[49] For a different series of carbon acids Galezowski et al. report $^{D}\Delta^{A}pK_a^{CH}$ values between 12.1 and 13.1[50] One may express $^{D}\Delta^{A}pK_a^{CH}$ by

$$^{D}\Delta^{A}pK_a^{CH} = \log {}^{D}\gamma^{A}_{C^-} + \log {}^{D}\gamma^{A}_{H^+} - \log {}^{D}\gamma^{A}_{CH} \qquad (13)$$

which is analogous to eq 12. Again, as is the case for the comparison between pure acetonitrile and aqueous acetonitrile, the dominant contribution to the solvent effect on the pK_a^{CH} comes from the much weaker solvation of the proton in acetonitrile, i.e., $\log {}^{D}\gamma^{A}_{CH} = 11.4$.[51]

Comparison with Carboxylic Esters. Fischer carbene complexes share a number of characteristics with carboxylic esters; one of them is that both have acidic properties. However, the acidity of Fischer carbene complexes is much higher. For example, the pK_a^{CH} of ethyl acetate in water is 25.6[52] (eq 14)



$$O{=}C(OCH_2CH_3)(CH_3) + H_2O \rightleftharpoons {}^{-}O{-}C(OCH_2CH_3){=}CH_2 + H_3O^+ \qquad (14)$$

while that for **3-Cr** in 50% MeCN-50% water is 12.98.[8] The pK_a^{CH} of ethyl acetate in acetonitrile is not known but it may be estimated as follows. Bordwell et al.[53] measured a pK_a^{CH} of 22.7 for $PhCH_2COOEt$ in DMSO from which they estimated a pK_a^{CH} of 30−31 for ethyl acetate in the same solvent. Assuming a $^{D}\Delta^{A}pK_a^{CH}$ of 11−12 for the difference in pK_a^{CH} between acetonitrile and DMSO (see previous section), one comes up with a pK_a^{CH} of 41−43 for CH_3COOEt in acetonitrile. This is about 18−20 pK_a^{CH} units higher than the pK_a^{CH} of **3-Cr** in acetonitrile; it compares with a difference of 12.6 pK_a units between **3-Cr** and ethyl acetate in aqueous solution. The smaller solvent effect on the pK_a^{CH} of **3-Cr** compared to that of ethyl acetate may be attributed to a stronger contribution of hydrogen-bonding solvation of the ethyl acetate anion compared to **3-Cr**$^-$ in the aqueous solvent.

Conclusions

(1) The ionization of several Fischer carbene complexes in the presence of TMG or BEMP (for **10-Cr**) has allowed the determination of pK_a^{CH} values in pure acetonitrile based on the free ion model of eqs 9 and 10.

(2) For the compounds that allow such comparison, the pK_a^{CH} values in pure acetonitrile are, on average, 10.2 units higher than in 50% MeCN−50% water. This difference is mainly the result of the much weaker solvation of the hydrogen ion in pure acetonitrile.

(3) By and large the *relative* acidities of the carbene complexes are the same in pure and aqueous acetonitrile except that **6-Cr**, which is a stronger acid than **1-Cr** in 50% MeCN−50% water, is somewhat weaker than **1-Cr** in pure acetonitrile and that **5-Cr** which is a much stronger acid than **4-Cr** in aqueous acetonitrile becomes less so in pure acetonitrile. These changes are attributed to a reduction of the acidifying hyperconjugative stabilization of the respective anions.

(4) The pK_a^{CH} value of **8-Cr** is too high to allow its determination by the bases used in this study; however, the estimated lower limit of this pK_a^{CH} is reasonable in the light of the pK_a^{CH} value in DMSO. On the other hand, the reduced π-donor effect of the aziridinyl group lowers the pK_a of **10-Cr** enough to bring it into a measurable range.

(5) The relative acidities of **1-Cr**, **4-Cr**, **5-Cr**, and **12-Cr** in THF do not match very well with those in acetonitrile or aqueous acetonitrile; this is most likely the result of strong ion-pairing effects in THF.

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Supporting Information Available: Tables S1−S9, raw data for equilibrium constant determinations; appendix describing ion-pair model (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[48] D stands for DMSO.

[49] (a) Keeffe, J. R.; Morey, J.; Palmer, C. A.; Lee, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1295. (b) Gandler, J. R.; Bernasconi, C. F. *J. Am. Chem. Soc.* **1992**, *114*, 631.

[50] Galezowski, W.; Stanczyk, M.; Jarczewski, A. *Can. J. Chem.* **1997**, *75*, 285.

[51] Based on $^{D}\Delta^{A}G^{o}_{tr} = 15.5$.[40]

[52] Amyes, T. L.; Richard, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 3129.

[53] Bordwell, F. G.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 4327.