Physical Organic Chemistry of Transition Metal Carbene Complexes. 8.[1] Kinetic and Thermodynamic Acidities of Alkoxyalkylcarbene Pentacarbonyl Complexes of Cr, Mo, and W in Aqueous Acetonitrile. Dependence on Metal, Alkyl Group, and Alkoxy Group

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A study of the acidity of various Fischer-type (alkoxyalkylcarbene)pentacarbonylmetal complexes and of their rates of deprotonation by OH⁻ and amines in 50% acetonitrile−50% water at 25 °C is reported. The pK_a values of $(CO)_5M=C(OMe)CH_3$ for M = W (12.36) and M = Mo (12.81) are quite comparable to that for M = Cr (12.50) determined previously, and the pK_a of $(CO)_5W=C(OMe)CH_2Ph$ (10.18) is similar to that of the chromium analog (10.40) reported earlier. These results indicate that the stabilization of the negative charge of the anion by the $(CO)_5M$ moiety depends little on the metal. The pK_a of $(CO)_5Cr=C(OEt)CH_3$ (12.98) is 0.48 units higher than that of the methoxy analog; this increase probably reflects an enhanced stabilization of the zwitterionic resonance structure of the carbene complex, $(CO)_5Cr^-C(=O^+Et)CH_3$, by the stronger electron-donating effect of the ethyl group. Intrinsic rate constants for the deprotonation of the carbene complexes by OH⁻ (k_o^{OH}) were estimated based on the Marcus equation, and intrinsic rate constants for the deprotonation of some of the carbene complexes by amines (k_o^B) were determined from Brønsted plots. The dependence of k_o^{OH} and k_o^B on the metal is rather small and hardly significant, except possibly for the reaction of $(CO)_5W=C(OMe)CH_3$ with secondary amines, for which k_o^B appears to be lower for the tungsten complex than for the chromium and molybdenum derivatives; k_o^{OH} for $(CO)_5Cr=C(OEt)CH_3$ is the same as for the methoxy analog.

In a recent paper, we reported the kinetic and thermodynamic acidities of (methoxymethylcarbene)-pentacarbonylchromium(0), MeO-Cr-Me, and (benzyl-methoxycarbene)pentacarbonylchromium(0), MeO-Cr-Bz, in 50% acetonitrile-50% water (v/v) at 25 °C.[2] The

MeO-Cr-Me   **MeO-Cr-Bz**

pK_a values, found to be 12.50 (MeO-Cr-Me) and 10.40 (MeO-Cr-Bz), respectively, demonstrate the powerful electron-withdrawing effect of the $(CO)_5Cr$ moiety. This electron-withdrawing effect is much stronger than that of a carbonyl group, as indicated by a comparison with the pK_a of 25.6 for methylacetate in aqueous solution.[3]

The determination of rate constants for the reversible deprotonation of these metal carbene complexes by primary aliphatic and secondary alicyclic amines, and also by carboxylate ions in the case of MeO-Cr-Me, allowed the calculation of *intrinsic* rate constants, k_o, for the proton transfers to these bases. The intrinsic rate constant of a reaction with a forward rate constant k_1 and a reverse rate constant k_{-1} is defined as $k_o = k_1 = k_{-1}$ when the equilibrium constant $K_1 = 1$ ($\Delta G° =$

0).[4] The intrinsic rate constants for carbene complex deprotonation fall within the typical range for proton transfer from carbon acids that lead to carbanions stabilized by moderately strong resonance effects.[6] For example, log k_o = 3.70 for the deprotonation of MeO-Cr-Me by secondary alicyclic amines is close to log k_o for the deprotonation of 2,3,4,5-tetrachlorocyclo-pentadiene[7a] (log k_o = 3.59) or (2,4-dinitrophenyl)-acetonitrile[7b] (log k_o = 3.70) by the same amines in 50% Me₂SO−50% water at 20 °C. Because intrinsic rate constants of proton transfers from carbon acids show a strong inverse correlation with the degree of resonance stabilization in the resulting anion,[6,8] the above results suggest that the extent of resonance stabilization in the conjugate base of MeO-Cr-Me may be comparable to that in the anions derived from 2,3,4,5-tetrachlorocy-clopentadiene or (2,4-dinitrophenyl)acetonitrile. This resonance stabilization probably arises from a strong contribution of the resonance structure **b**, coupled with
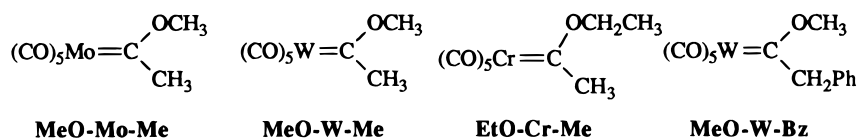
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(1) Part 7: Bernasconi, C. F.; Flores, F. X.; Kittredge, K. *J. Am. Chem. Soc.* **1997,** *119,* 2103.
(2) Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **1993,** *115,* 12526.
(3) Amyes, T. L.; Richard, J. P. *J. Am. Chem. Soc.* **1996,** *118,* 3129.

(4) For a proton transfer from a carbon acid to a buffer base, CH + B^v ⇌ C⁻ + BH^{v+1}, it is common to include statistical factors[5] for the number of equivalent basic sites on B^v(q) and the number of equivalent protons on BH^{v+1}(p) so that $k_o = k_1/q = k_{-1}/p$ when $pK_a^{BH} − pK_a^{CH} + \log(p/q) = 0$.
(5) Bell, R. P. *The Proton in Chemistry,* 2nd ed.; Cornell University: Ithaca, NY, 1973; Chapter 10.
(6) For a recent review, see: Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992,** *27,* 119.
(7) (a) Bernasconi, C. F.; Stronach, M. W. *J. Am. Chem. Soc.* **1990,** *112,* 8448. (b) Bernasconi, C. F.; Hibdon, S. A. *J. Am. Chem. Soc.* **1983,** *105,* 4343.
(8) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987,** *20,* 301. (b) Bernasconi, C. F. *Acc. Chem. Res.* **1992,** *25,* 9.

Chart 1

MeO-Mo-Me   MeO-W-Me   EtO-Cr-Me   MeO-W-Bz

additional charge delocalization into the CO ligands. As
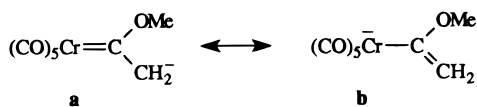
elaborated upon elsewhere,[6,8] the main reason for the low intrinsic rate constants in reactions leading to resonance-stabilized carbanions is that there is a lag in the charge delocalization behind proton transfer at the transition state ("transition state imbalance").

In the present paper, we explore the effect of changing the metal from Cr to Mo and W and of changing the alkoxy group from methoxy to ethoxy on the pK_a and the rates of proton transfer.

As with the reactions of MeO-Cr-Me and MeO-Cr-Bz, the proton transfer is followed by acid-catalyzed hydrolytic breakdown of the conjugate anion of the carbene complex, which leads to the corresponding aldehyde or a mixture of the aldehyde and the corresponding vinyl ether.[9] This is shown in Scheme 1, where k_1, k_{-1}, and

Scheme 1
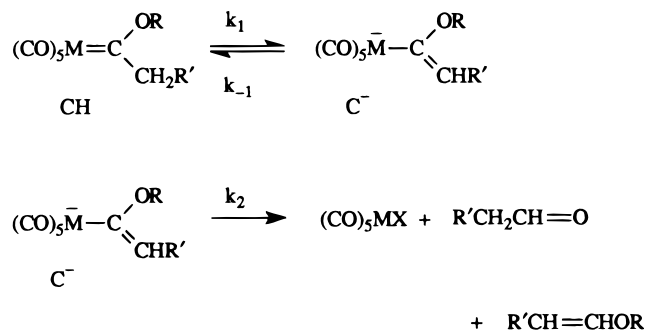
k_2 are defined by eqs 1−3 and X can be OH^-, B, or the solvent. The detailed mechanism of the hydrolytic step,

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

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

$$k_2 = k_2^{H}a_{H^+} + k_2^{H_2O} + k_2^{BH}[BH] \quad (3)$$

which most likely involves rate-limiting protonation of the carbene carbon of C^- concerted with C−M bond cleavage to generate the vinyl ether as the initial product, has been discussed elsewhere.[9]

Results

General Features. The carbene complexes shown in Chart 1 were investigated. When MeO-Mo-Me, MeO-W-Me, EtO-Cr-Me, or MeO-W-Bz is placed into a basic solution, it behaves in a similar manner as MeO-Cr-Me. Two reactions are observed. The faster of the two
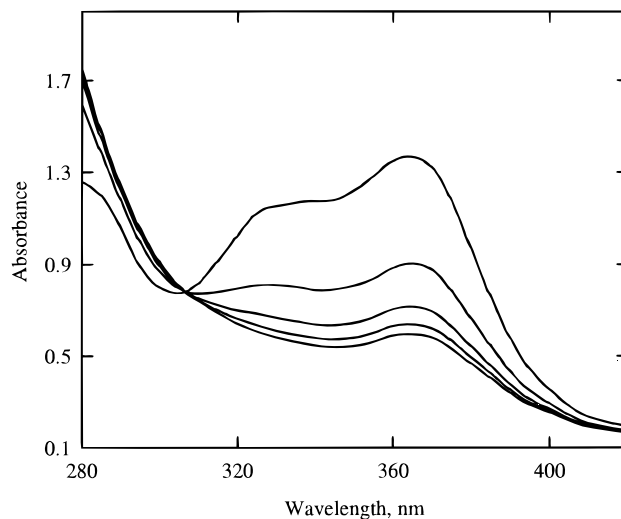
(9) (a) Bernasconi, C. F.; Flores, F. X.; Sun, W. *J. Am. Chem. Soc.* **1995**, *117*, 4875. (b) Bernasconi, C. F.; Sun, W. *Organometallics* **1995**, *14*, 5615.

Figure 1. Time-resolved spectra of the deprotonation of MeO-Mo-Me with 0.1 M KOH ($[CH]_o = 1.90 \times 10^{-4}$ M). The first spectrum was obtained within 1.25 ms after mixing. Subsequent spectra were taken 50, 100, 150, and 250 ms, respectively, after mixing.
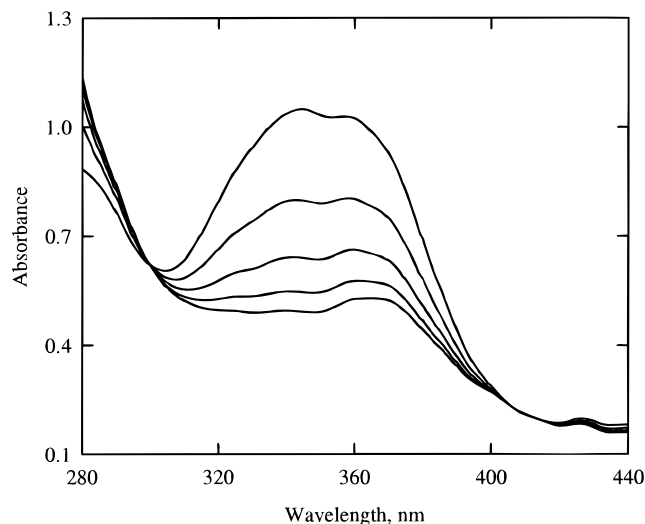

Figure 2. Time-resolved spectra of the deprotonation of MeO-W-Me with 0.1 M KOH ($[CH]_o = 1.30 \times 10^{-4}$ M). The first spectrum was obtained 1.25 ms after mixing and subsequent spectra at 20 ms intervals.

represents reversible deprotonation, the slower one hydrolytic decomposition, as shown in Scheme 1. Time-resolved spectra referring to the deprotonation by OH^- are shown in Figure 1 for MeO-Mo-Me and in Figure 2 for MeO-W-Me; the spectra for EtO-Cr-Me (not shown) are very similar to those for MeO-Cr-Me published previously.[2]

Reversibility of the proton transfer was established by reacting the anion with HCl or an amine buffer, which regenerates the carbene complex. Because of the relatively rapid hydrolytic decomposition of the anion (half-lives of a few seconds), the reaction of the anion with acid had to be initiated in a double-mixing stopped-

Table 1. Summary of pK_a^{CH}, k_1^{OH}, $k_{-1}^{H_2O}$, $k_2^{H_2O}$ Values for Various Carbene Complexes in 50% Acetonitrile−50% Water at 25 °C[a]

entry	carbene complex	pK_a^{CH}	k_1^{OH} ($M^{-1} s^{-1}$)	$k_{-1}^{H_2O}$ (s^{-1})	$k_2^{H_2O}$ (s^{-1})
1	$(CO)_5W=C(OMe)CH_3$	12.36	284	0.42	2.5×10^{-2}
2	$(CO)_5Mo=C(OMe)CH_3$	12.81	181	0.75	3.7×10^{-3}
3	$(CO)_5Cr=C(OMe)CH_3$	12.50^b	456^b	0.91^b	0.16^c
4	$(CO)_5Cr=C(OEt)CH_3$	12.98	241	2.48	0.29^c
5	$(CO)_5W=C(OMe)CH_2Ph$	10.18	140	1.35×10^{-3}	7.3×10^{-3} ^{d}
6	$(CO)_5Cr=C(OMe)CH_2Ph$	10.40^b	115^b	1.90×10^{-3} ^{b}	8.5×10^{-3} ^{d}

^{a} μ = 0.1 M (KCl); estimated uncertainties in the pK_a^{CH} values are ±0.06; estimated uncertainties in the k_1^{OH} and $k_2^{H_2O}$ values are ±6% or better, in the $k_{-1}^{H_2O}$ values, ±10% or better. ^{b} Reference 2. ^{c} Reference 9a. ^{d} Reference 9b.
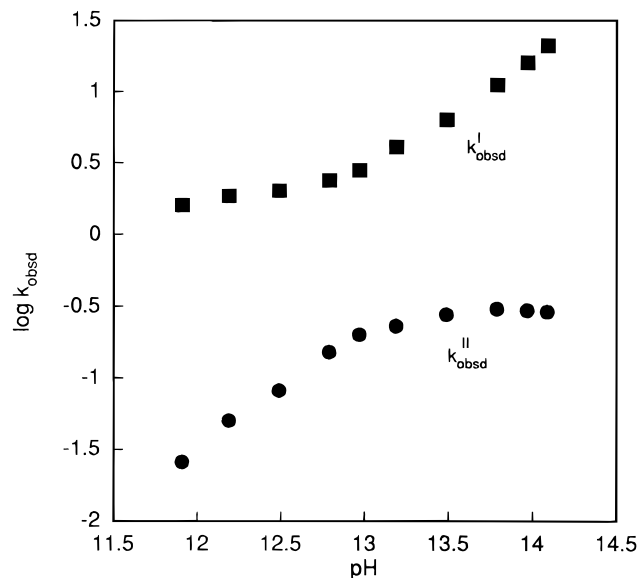

Figure 3. Plots of log k_{obsd}^I and log k_{obsd}^{II} *vs* pH for the reaction of EtO-Cr-Me with KOH. Data for k_{obsd}^{II} are from ref 9a.

flow apparatus within about 100−150 ms after formation of the anion. Under these conditions, the original carbene complex was virtually completely recovered, as confirmed by its UV spectrum; longer delays of the reaction with acid led to incomplete recovery of the carbene complex.

Kinetics. All experiments were performed in 50% acetonitrile−50% water (v/v) at 25 °C and an ionic strength of 0.1 M maintained with KCl. Rates were measured in KOH solutions and, for some carbene complexes, in a number of amine buffers. Pseudo-first-order conditions, with the carbene complexes as minor component, were used throughout.

EtO-Cr-Me, MeO-Mo-Me, and MeO-W-Me. For these carbene complexes, the pseudo-first-order rate constants for the proton transfer (k_{obsd}^I) and the hydrolytic cleavage (k_{obsd}^{II}) are well-separated under all reaction conditions. This can be seen from the plots of log k_{obsd}^I and log k_{obsd}^{II} *vs* pH for the reaction of EtO-Cr-Me with KOH, shown in Figure 3, which are representative for $(CO)_5M=C(OR)CH_3$-type complexes (M = Cr, Mo, W). On the basis of Scheme 1, k_{obsd}^I and k_{obsd}^{II} are given by eqs 4 and 5, respectively,[10] with K_a^{CH} being

$$k_{obsd}^I = k_1^{OH}[OH^-] + k_{-1}^{H_2O} \qquad (4)$$

$$k_{obsd}^{II} = \frac{K_a^{CH}}{K_a^{CH} + a_{H^+}} k_2^{H_2O} \qquad (5)$$

the acid dissociation constant of the carbene complex.

The raw data for EtO-Cr-Me are summarized in Table S1 of the supporting information[11] whereas the k_1^{OH}, $k_{-1}^{H_2O}$, and $k_2^{H_2O}$ values are reported in Table 1; from $k_1^{OH}/k_{-1}^{H_2O} = K_1^{OH} = K_a^{CH}/K_w$,[12] one also obtains $K_a^{CH} = 1.05 \times 10^{-3}$ ($pK_a^{CH} = 12.98$). Similar data for MeO-Mo-Me and MeO-W-Me are summarized in Table S2[11] and Table 1.

Rates of proton transfer involving amine bases were determined by means of pH-jump experiments. In these experiments, the anion (C^- in Scheme 1) was first generated by reaction of CH with KOH (typically [KOH] = 0.08 M) in a double-mixing stopped-flow apparatus. After an incubation time of 0.5−0.8 s, the solution containing C^- was mixed with a 1:1 amine buffer in the same apparatus. The incubation time was long enough to ensure virtual completion of the proton transfer, but short enough to minimize hydrolytic cleavage of the anion (k_2-step in Scheme 1). The raw data are summarized in Tables S3 and S4.[11] Plots of k_{obsd}^I *vs* [B] were linear in all cases. For these experiments, k_{obsd}^I is given by eq 6, with B being the amine base. Hence, the slopes

$$k_{obsd}^I = k_1^{OH} + k_{-1}^{H_2O} + k_1^B[B] + k_{-1}^{BH}[BH^+] \quad (6)$$

of these plots are given by eq 7,[13] with K_a^{BH} being the

$$\text{slope} = k_1^B + k_{-1}^{BH}\frac{a_{H^+}}{K_a^{BH}} = k_1^B\left(1 + \frac{a_{H^+}}{K_a^{CH}}\right) \qquad (7)$$

acidity constant of the protonated amine; the k_1^B and k_1^{BH} values calculated from these slopes are reported in Table 2.

MeO-W-Bz. The methodology used for MeO-W-Bz was quite similar to that described above for EtO-Cr-Me, MeO-Mo-Me, and MeO-W-Me. However, the substantially higher acidity of MeO-W-Bz precluded a determination of the pK_a^{CH} from the $k_1^{OH}/k_{-1}^{H_2O}$ ratio. The problem is that even though k_1^{OH} is easily obtained from the slope of a plot of k_{obsd} *vs* [OH^-] at relatively high [OH^-] (raw data in Table S1),[11] $k_{-1}^{H_2O}$ cannot be determined from the intercept of this plot. There are two reasons for this. One is that at KOH concentrations low enough to make $k_{-1}^{H_2O}$ comparable to $k_1^{OH}[OH^-]$ ([OH^-] ≈ 10^{-5} M), the solutions have insufficient buffer capacity for reliable pH-control and hence the error in k_{obsd} becomes too large. The other is that at such low [OH^-], the relationship $k_{obsd}^I \gg k_{obsd}^{II}$ breaks down because $k_{-1}^{H_2O} < k_2^{H_2O}$ so that eq 4 is no longer valid.

(10) In basic solution, the $k_1^{H_2O}$, $k_1^{H_2O}a_{H^+}$, and $k_2^H a_{H^+}$ terms are negligible.
(11) See the paragraph concerning Supporting Information at the end of this paper.
(12) pK_w = 15.19.[2]
(13) $k_{-1}^{BH}a_{H^+}/K_a^{BH}$ converts to $k_1^B a_{H^+}/K_a^{CH}$ by virtue of the relationship $k_1^B/k_{-1}^{BH} = K_a^{CH}/K_a^{BH}$.

**Table 2. Summary of Rate Constants for
Reversible Deprotonation of Various Carbene
Complexes by Amines in 50% Acetonitrile−50%
Water at 25 °C[a]**

amine	pK_a^{BH}	k_1^B (M^{-1} s^{-1})	k_{-1}^{BH} (M^{-1} s^{-1})
$(CO)_5Mo=C(OMe)CH_3$ ($pK_a^{CH} = 12.81$)			
piperidine	11.01	521	3.23×10^4
piperazine	9.97	129	8.91×10^4
n-BuNH$_2$	10.40	63.5	1.63×10^4
MeOCH$_2$CH$_2$NH$_2$	9.39	15.9	4.17×10^4
$(CO)_5W=C(OMe)CH_3$ ($pK_a^{CH} = 12.36$)			
piperidine	11.01	461	1.08×10^4
piperazine	9.97	207	5.11×10^4
HEPA[b]	9.33	70.7	7.61×10^4
morpholine	8.70	35.7	1.64×10^5
n-BuNH$_2$	10.40	61.4	6.36×10^3
MeOCH$_2$CH$_2$NH$_2$	9.39	14.0	1.31×10^4
$(CO)_5Cr=C(OMe)CH_3$[c] ($pK_a^{CH} = 12.50$)			
piperidine	11.01	906	2.77×10^4
piperazine	9.97	246	8.23×10^4
HEPA[b]	9.33	85.5	1.25×10^5
n-BuNH$_2$	10.40	122	1.52×10^4
MeOCH$_2$CH$_2$NH$_2$	9.39	22.6	2.88×10^4
$(CO)_5W=C(OMe)CH_2Ph$ ($pK_a^{CH} = 10.18$)			
piperidine	11.01	358	52.7
piperazine	9.97	98.0	158
HEPA[b]	9.33	38.5	271
morpholine	8.70	34.2	1.03×10^3
n-BuNH$_2$	10.40	133	80
MeOCH$_2$CH$_2$NH$_2$	9.39	19.6	12.0
H$_2$NCOCH$_2$NH$_2$	8.14	3.26	352
NCCH$_2$NH$_2$	5.29	0.26	2.0×10^4
$(CO)_5Cr=C(OMe)CH_2Ph$[c] ($pK_a^{CH} = 10.40$)			
piperidine	11.01	225	55
piperazine	9.97	74.8	200
HEPA[b]	9.33	25.2	295
morpholine	8.70	19.5	978
n-BuNH$_2$	10.40	75.5	75.5
MeOCH$_2$CH$_2$NH$_2$	9.39	16.1	165
H$_2$NCOCH$_2$NH$_2$	8.14	2.30	413
NCCH$_2$NH$_2$	5.29	0.126	1.61×10^4

[a] $\mu = 0.1$ M (KCl). [b] HEPA = *N*-(2-hydroxyethyl)piperazine. [c] Reference 2.

The pK_a^{CH} could, however, be determined from kinetic experiments in piperazine buffers at different pH values (Table S5).[11] In these and other amine buffers, the relationship $k_{obsd}^I \gg k_{obsd}^{II}$ is restored because $k_{-1}^{BH} \gg k_2^{BH}$ and hence eq 6 is valid. Figure 4 shows a plot of buffer-plot slopes (Table S6)[11] *vs* a_{H^+} according to eq 7, from which k_1^B (Table 2) and pK_a^{CH} (Table 1) were obtained. The raw data with other amine buffers are summarized in Table S7.[11]

Discussion

As was already the case for MeO-Cr-Me and MeO-Cr-Bz, the pK_a^{CH} of the various carbene complexes studied in the present work could not be determined by classical spectrophotometric methods. This is a consequence of rapid hydrolysis of the anion C$^-$, which necessitated a *kinetic* determination of the thermodynamic acidity of CH. This kinetic determination was relatively straightforward for MeO-Mo-Me, MeO-W-Me, and EtO-Cr-Me because, as was the case for MeO-Cr-Me, the proton-transfer equilibrium is rapidly established compared to the hydrolysis of C$^-$. This is true both in the presence and absence of buffers. Of particular significance is the fact that $k_{-1}^{H_2O} \gg k_2^{H_2O}$ (Table 1), which allows a direct determination of $k_{-1}^{H_2O}$ from kinetic measurements in KOH solutions and hence a determination of pK_a^{CH} from the $k_1^{OH}/k_{-1}^{H_2O}$ ratio.
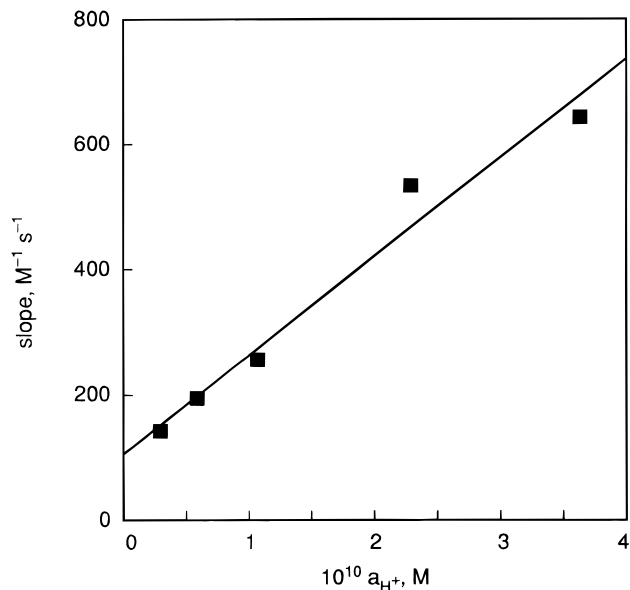

Figure 4. Plot of buffer plot slopes *vs* a_{H^+} according to eq 7 for the reaction of MeO-W-Bz with piperazine.

For MeO-W-Bz, we have $k_{-1}^{H_2O} \ll k_2^{H_2O}$, as is the case for MeO-Cr-Bz,[2,9b] and, hence, it was not possible to determine $k_{-1}^{H_2O}$ and to find pK_a^{CH} from kinetic data in KOH solution. However, in amine buffers, the proton transfer equilibrium *is* rapidly established compared to the hydrolysis and, hence, pK_a^{CH} could be determined via eq 7 (B = piperazine).

Effect of the Metal. The main conclusion is that both the thermodynamic and kinetic acidities of Fischer carbenes appear to be remarkably insensitive to the metal. This is seen from comparisons of $(CO)_5M=C$-$(OMe)CH_3$, where M = Cr, Mo, and W, and of $(CO)_5$-$M=C(OMe)CH_2Ph$, where M = Cr and W (Table 1). For example, the difference between the most acidic methoxymethylcarbene complex (W) and the least acidic one (Mo) is only 0.45 pK units, while the pK_a^{CH} of MeO-W-Bz is only 0.22 units lower than that of MeO-Cr-Bz. With respect to the rate constants for deprotonation of the carbene complexes, the k_1^{OH} and k_1^B values for the methoxymethylcarbene complexes differ by only ∼2.5-fold and ∼2-fold, respectively, while for the benzylmethoxycarbene complexes, the differences in k_1^{OH} and k_1^B are even smaller.

There are, however, some subtle differences between the order of the thermodynamic and kinetic acidities of the methoxymethylcarbene complexes which are worth pointing out. For the equilibrium acidities we have W > Cr > Mo, for k_1^{OH} the order is Cr > W > Mo, and for k_1^B it is Cr > W ≈ Mo. These differences between the kinetic and thermodynamic order must be a consequence of a slight dependence of the intrinsic rate constants on the metal. For the proton transfers to amines, logarithmic values of the intrinsic rate constants are summarized in Table 3. They were obtained from Brønsted plots such as shown in Figure 5.[14] Table 3 also includes approximate log k_o values for the deprotonation by OH$^-$; they were estimated as log $k_o =$ log $k_1^{OH} - 0.5$ log K_1^{OH}.[15]

(14) Figure 5 only includes Brønsted plots for cases where k_1^B was determined for more than two amines. The Brønsted plots are based on statistically corrected k_1^B and ΔpK_a value where q is the number of equivalent basic sites on B and p is the number of equivalent protons on BH$^+$.

Table 3. Intrinsic Rate Constants and Brønsted β Values for Proton Transfer from $(CO)_5M=C(OMe)CH_3$ and $(CO)_5M=C(OMe)CH_2Ph$ to Amines and OH^{-} [a]

	carbene complex	pK_a^{CH}	primary RNH_2		secondary R_2NH		OH^{-}
			β	$\log k_o^{B}$	β	$\log k_o^{B}$	$\log k_o^{OH}$
1	$(CO)_5W=C(OMe)CH_3$	12.36	0.64	2.73	0.49 ± 0.01	3.18 ± 0.02	~ 1.09
2	$(CO)_5Mo=C(OMe)CH_3$	12.81	0.59	2.95	0.68	3.73	~ 1.07
3	$(CO)_5Cr=C(OMe)CH_3^{b}$	12.50	0.61 ± 0.06	3.04 ± 0.17	0.62 ± 0.03	3.70 ± 0.07	~ 1.31
4	$(CO)_5Cr=C(OEt)CH_3$	12.98					~ 1.38
5	$(CO)_5Cr=C(OMe)CH_2Ph^{b}$	10.40	0.54 ± 0.04	1.51 ± 0.10	0.48 ± 0.07	1.86 ± 0.07	~ -0.33
6	$(CO)_5W=C(OMe)CH_2Ph$	10.18	0.51 ± 0.07	1.55 ± 0.16	0.47 ± 0.10	1.93 ± 0.09	~ -0.36

[a] Error limits are standard deviations based on Brønsted plots. No standard deviations given for β and $\log k_o^{B}$ for $(CO)_5Mo=C(OMe)CH_3$ and $(CO)_5W=C(OMe)CH_3$ because Brønsted plots are based on two amines only, but experimental uncertainty in these β and $\log k_o^{B}$ values are likely to be similar to those for the other compounds. [b] Reference 2.
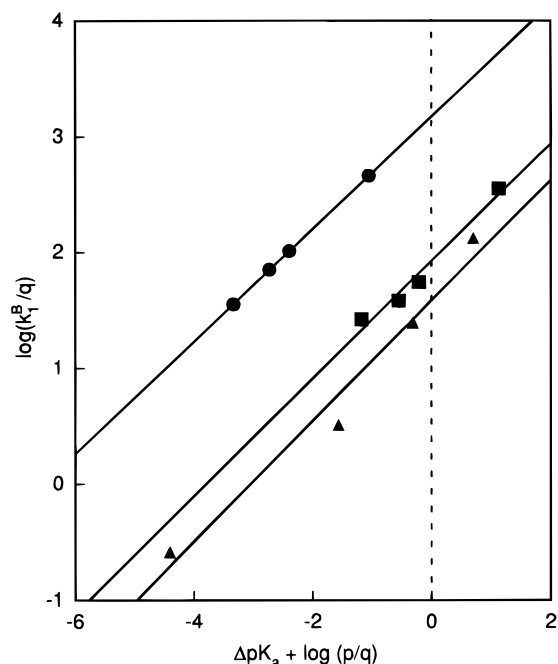

Figure 5. Brønsted plots for the deprotonation of MeO-W-Me by secondary alicyclic amines (●) and for the deprotonation of MeO-W-Bz by secondary alicyclic (■) and primary aliphatic amines (▲). The points of intersection of the Brønsted lines with the vertical dashed line correspond to $\log k_o^{B}$.
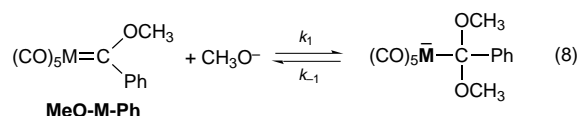
Because the dependence of the various $\log k_o$ values on the metal is so small, the differences that do exist should be interpreted with caution, especially because some of the $\log k_o$ values are subject to a relatively large experimental uncertainty. In the case of $\log k_o^{OH}$, because of their approximate nature, no interpretation of their small metal dependence will be attempted.

Regarding the amine reactions, the fact that the $\log k_o^{B}$ values for MeO-Cr-Me and MeO-Mo-Me are the same within experimental error indicates that the higher k_1^{B} values for MeO-Cr-Me compared to those of MeO-Mo-Me are merely a consequence of the higher equilibrium acidity of the chromium complex. Conversely, the fact that the $\log k_o^{B}$ values for MeO-W-Me are lower than those for MeO-Cr-Me explains why deprotonation of MeO-W-Me by a given amine (k_1^{B}) is slower than that of MeO-Cr-Me, despite the higher acidity of MeO-W-Me.

The reasons for the lower intrinsic rate constants for the tungsten complex are unclear. If a steric effect were involved, due to the larger size of W^{17} and, hence, presumably of the $W(CO)_5$ moiety compared to the $Cr(CO)_5$ moiety, one would expect the steric effect also to be reflected in a lower $\log k_o^{B}$ for MeO-W-Bz compared to MeO-Cr-Bz. And since the atomic radius of Mo is the same as that of $W,^{17}$ the $\log k_o^{B}$ values for MeO-Mo-Me should be closer to those for MeO-W-Me than those for MeO-Cr-Me. Neither of these expectations are met, however. Since the effect of the metal is so small anyway, further speculation seems unwarranted at this time.

The small dependence of pK_a^{CH} on the metal implies that the stabilization of C^- by the $(CO)_5M$ moiety is very similar for the three metals. This stabilization presumably results from a combination of an inductive and a resonance effect. With regard to the latter, on the basis of the well-known fact that intrinsic rate constants of reactions are strongly affected by resonance in either the reactant or product[6]—the more resonance the lower k_o—we infer from the small dependence of $\log k_o$ on the metal that the degree of resonance stabilization provided by the $(CO)_5M$ moiety also depends little on M.

It should be noted that our findings are similar to those in a study of methoxide ion addition to MeO-M-Ph (M = Cr and W).[18] The reaction yields an anionic tetrahedral intermediate, eq 8, with the rate and equilibrium constants being very similar for the two metals, again implying that the overall stabilization by the $(CO)_5M$ moiety as well as the resonance component of this stabilization is virtually independent of the metal. On the other hand, our results are seemingly

$$(CO)_5M=C \overset{OCH_3}{\underset{Ph}{\diagdown}} \; + \; CH_3O^- \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; (CO)_5\bar{M}-\overset{OCH_3}{\underset{OCH_3}{C}}-Ph \quad (8)$$

MeO-M-Ph

in marked contrast to the large dependence of the pK_a values of metal hydrido complexes of the type $(\eta^5-C_5H_5)M(CO)_3H.^{19}$ In acetonitrile, these pK_a values are 13.3 for M = Cr, 13.9 for M = Mo, and 16.1 for M = W; in methanol, the respective pK_a values are 6.4, 7.2, and 9.0. This trend in the pK_a values of the metal hydrido complexes would be difficult to reconcile with our results if it were assumed that these pK_a values reflect a strong

(15) This is equivalent to applying the simplest version of the Marcus[16] equation, $\Delta G^{\ddagger} = \Delta G_o^{\ddagger} + 0.5\Delta G^{\circ} + (\Delta G^{\circ})^2/16\Delta G_o^{\ddagger}$, and neglecting the third term which is very small in our case.

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increase in the stabilization of the anions, $(\eta^5\text{-}C_5H_5)M^-$-$(CO)_3$, along the series W < Mo < Cr. However, Norton[19b] has shown that the differences in the acidities of the metal hydrido complexes are *not* due to differences in the stabilization of the anions, but can be traced to differences in the M−H bond-dissociation enthalpies of the hydrido complexes. In other words, there is no contradiction between Norton's and our results.

Effect of the Alkoxy Group. The comparison of EtO-Cr-Me with MeO-Cr-Me shows that the change from a methoxy to an ethoxy group increases the pK_a^{CH} by almost 0.5 units (Table 3). This increase may, in principle, arise from a destabilization of the anion, a stabilization of the neutral carbene complex by the change from methoxy to ethoxy, or a combination of the two effects. Inasmuch as the resonance structure **c** appears to play a dominant role in the stabilization of carbene complexes,[20] the increase in pK_a^{CH} is most
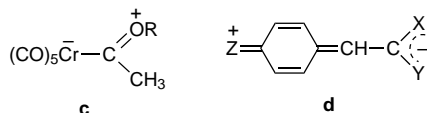

plausibly attributed to increased stabilization of **c** by stronger electron donation when R = ethyl instead of methyl.

With respect to the kinetic acidity, approximately half of the decrease in the thermodynamic acidity is expressed in a decrease of k_1^{OH}. This means that the intrinsic rate constant, k_0^{OH}, for the ethoxy carbene complex differs little from that of the methoxy analog (Table 3). In view of the above explanation for the decreased acidity of the ethoxy complex, it may seem surprising that k_0^{OH} is nearly independent of the alkoxy group. This is because the increased resonance stabilization of the ethoxy complex is expected to reduce the intrinsic rate constant.[21] However, another consequence of the extra stabilization of **c** is that it enhances the **c**-character of the carbene complex, thereby preorganizing its electronic structure in the $(CO)_5Cr$ moiety toward that of the anion. This preorganization is likely to stabilize the transition state by facilitating the delocalization of the incipient negative charge into the $(CO)_5Cr$ moiety, i.e., by reducing the degree by which the charge delocalization into the $(CO)_5Cr$ moiety lags behind proton transfer (transition state imbalance) and, hence, to increase k_0^{OH} for the ethoxy derivative. This will counteract the k_0^{OH} lowering effect of the enhanced resonance stabilization of the neutral carbene complex.

This kind of competition between k_0-lowering resonance effects and k_0-enhancing preorganization has been observed in nucleophilic additions to olefinic substrates of the type shown in eq 9, where X, Y are $(CH=O)_2$,[22] $(CN)_2$,[23] (H,NO_2),[24] and others[25] and where

Z = H is being compared with π-donor substituents such as MeO or Me_2N. In some cases, the k_0-lowering
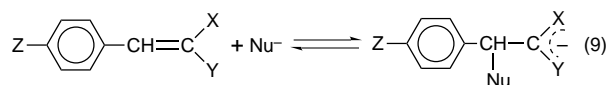
resonance effect by the π-donor (resonance structure **d**) dominates so that there is a net decrease in k_0 (X, Y: $(CH=O)_2$ in water, $(CN)_2$ in water, and H, NO_2 in 90% Me_2SO−10% water); in other cases, the opposite is true (X, Y: H, NO_2 in water); finally, with H, NO_2 in 50% Me_2SO−50% water, the two effects just about offset each other. The latter situation seems to prevail in the deprotonation of (alkoxymethylcarbene)pentacarbonyl-chromium(0) complexes.

Effect of the Benzyl Group. Comparison of MeO-W-Bz with MeO-W-Me shows an acidifying effect of 2.18 pK_a units, which is nearly identical to that for MeO-Cr-Bz relative to MeO-Cr-Me ($\Delta pK_a^{CH} = 2.10$). The intrinsic rate constants for proton transfer from MeO-W-Bz are substantially lower than those for the methyl derivatives: $\Delta \log k_0 = -1.18$ (primary RNH_2), -1.25 (secondary R_2NH), and -1.45 (OH^-). These reductions in k_0 are somewhat smaller than, but still quite comparable to, those found in comparing MeO-Cr-Bz with MeO-Cr-Me: $\Delta \log k_0 = -1.43$ (primary RNH_2), -1.84 (secondary R_2NH), and -1.64 (OH^-). Both the increased acidity and the reduction in the intrinsic rate constants can be attributed to the enhanced resonance stabilization of the anion derived from the benzyl derivatives, as described in more detail elsewhere.[2]

We also note that the difference between $\log k_0^B$(secondary R_2NH) and $\log k_0^B$(primary RNH_2) for the reactions of the benzyl carbene complexes is smaller than that for the methyl carbene complexes. As discussed in some detail in ref 2, this suggests more steric crowding in the transition state for the deprotonation of the benzyl carbene complexes compared to that for the deprotonation of the methyl carbene complexes.

Conclusions

The dependence of the acidity of $(CO)_5M=C(OMe)$-CH_3-type carbene complexes on the metal is quite small, so is that of the intrinsic rate constants for proton transfer to OH^- and amines, except for the reaction of the W derivative for which k_0, especially with secondary amines, is somewhat lower than that for the Mo and Cr complexes. These findings suggest that the degree of resonance stabilization of C^- by the $(CO)_5M$ moiety depends little on the metal.

MeO-M-Bz complexes (M = Cr and W) are more acidic than the corresponding methyl derivatives, due to additional resonance stabilization of C^- by the phenyl group on the α-carbon. The fact that the intrinsic rate constants for proton transfer are substantially lower for the benzyl compared to the methyl derivatives again

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(21) Just as the intrinsic rate constant is reduced in reactions that lead to a resonance-stabilized product, it is reduced when a resonance-stabilized *reactant* undergoes a reaction. In the former case, the reduction in k_0 is a consequence of resonance development lagging behind charge transfer or bond formation at the transition state; in the latter, it is a consequence of resonance being lost ahead of charge transfer or bond formation.[6,8]

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provides evidence for transition state imbalance with resonance development lagging behind proton transfer.

EtO-Cr-Me is about 0.5 pK_a units less acidic than MeO-Cr-Me, but the intrinsic rate constant for proton transfer to OH$^-$ is nearly unchanged. The reduced acidity is attributed to enhanced stabilization of the resonance structure **c** when R = Et. The insensitivity of k_o^{OH} to the change in alkoxy group is most likely the result of a cancellation of the k_o^{OH}-lowering effect from the increased resonance stabilization of the ethoxy carbene complex, with a k_o^{OH}-enhancing preorganization effect of resonance structure **c**.

Experimental Section

Materials. Standard Schlenk techniques were used in synthesizing and handling the carbene complexes, with argon as the protecting gas. More details about synthetic procedures can be found in ref 26. MeO-W-Me and MeO-Mo-Me were synthesized according to the method of Aumann and Fischer[27] described for the synthesis of MeO-Cr-Me. For MeO-W-Me: mp 51.5−53 °C (lit. 52 °C);[28] ^{1}H NMR (250 MHz, CD$_3$CN) δ 2.89 (s, 3H, Me), 4.68 (s, 3H, MeO); IR (KBr) 2071 (CO), 1938 cm^{-1} (CO); UV/vis (50% MeCN−50% H$_2$O) λ_{max} 342 nm (log ϵ 3.90), shoulder at 365 nm. For MeO-Mo-Me: mp 38.5−40 °C; ^{1}H NMR (250 MHz, CD$_3$CN) δ 2.89 (s, 3H, Me), 4.68 (s, 3H, MeO); IR (KBr) 2071 (CO), 1939 cm^{-1} (CO); UV/vis (50% MeCN−50% H$_2$O) λ_{max} 366 nm (log ϵ 3.85), shoulder at 338 nm. MeO-W-Bz was synthesized following the method of Fischer et al.[29] described for the synthesis of MeO-Cr-Bz, mp 49−50 °C, ^{1}H NMR (250 MHz, CD$_3$CN) δ 4.50 (s, 2H, CH$_2$), 4.60 (s, 3H, OMe), 7.16−7.32 (m, 5H, Ph); ^{13}C NMR (300 MHz, CD$_3$CN) δ 333.1 (C=), 211.7, 204.8, 198.9, 198.1, 192.6 (CO), 136.4, 130.7, 129.5, 127.8 (Ph), 72.23 (OMe), 70.51 (CH$_2$). EI-MS (*m/z*) 458 (M$^+$, 78), 430 (26), 375 (59), 359 (68), 331 (100), 303 (59), 275 (42), 149 (45), 91 (62); IR (CD$_3$CN) 2070 (CO), 1922 cm^{-1} (CO); UV/vis (50% MeCN−50% H$_2$O) λ_{max} 370 nm (log ϵ 3.87), shoulder at 350 nm. EtO-Cr-Me was prepared as

described by Fischer and Maasböl:[30] mp 5−6 °C (lit 5 °C);[30] ^{1}H NMR (250 MHz, CD$_3$CN) δ 1.65 (t, 3H, *CH*$_3$CH$_2$O), 2.95 (s, 3H, CH$_3$), 5.01 (br s, 2H, CH$_3$*CH*$_2$O); IR (CD$_3$CN) 2061 (CO), 1981 (CO), 1938 cm^{-1} (CO); UV/vis (50% MeCN−50% H$_2$O) λ_{max} 370 nm (log ϵ 3.86).

Acetonitrile was refluxed over CaH$_2$ and distilled under argon. All amines were refluxed over NaOH and freshly distilled under argon prior to use. KOH and HCl solutions were prepared using "dilut it" from Baker Analytical. Water was taken from a Milli-Q water purification system.

Kinetic Runs and Spectra. The spectra shown in Figures 1 and 2 were obtained from the absorbance values of kinetic traces generated at 5 nm intervals in an Applied Photophysics DX.17MV stopped-flow apparatus equipped with a standard photomultiplier. Connecting the points and smoothing the curves was done by the computer software of the stopped-flow apparatus. The spectra of the recovered carbene complexes generated by reacting the amines with HCl or amine buffers were obtained by using the sequential mixing mode of the double-mixing stopped-flow apparatus. In these experiments, the anion was formed by reaction of the carbene complex with KOH in the first mixing event; the regeneration of the carbene complex was achieved by adding the acid to the anion solution in the second mixing event that was triggered within 100−150 ms of the formation of the anion.

The pH in 50% acetonitrile−50% water was determined from eq 10,[31] with pH$_{meas}$ being the pH measured by the pH meter calibrated with standard aqueous buffers. The pK_a

$$pH = pH_{meas} + 0.18 \qquad (10)$$

values of the various amines in 50% acetonitrile−50% water were determined previously.[2] The methodology for the kinetic runs was the same as described before[2] and is described in more detail in ref 26. All kinetic experiments were performed in the stopped-flow apparatus.

Supporting Information Available: Tables S1−S7, containing kinetic data (7 pages). Ordering information is given on any current masthead page.

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