

Physical Organic Chemistry of Transition Metal Carbene Complexes. 4.¹ Kinetics and Equilibria of Methoxide Ion Addition to [Methoxy(phenyl)carbene]pentacarbonylchromium(0) and [Methoxy(phenyl)carbene]pentacarbonyltungsten(0)

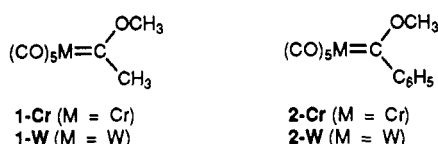
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Received October 22, 1993^o

A stopped-flow kinetic study of the reversible addition of methoxide ion to [methoxy(phenyl)carbene]pentacarbonylchromium(0) (**2-Cr**) and [methoxy(phenyl)carbene]pentacarbonyltungsten(0) (**2-W**) in methanol at 25 °C is reported. The reaction was investigated by approaching the equilibrium (eq 1) from either side; due to the rapid decomposition of the adduct, the reaction in the reverse direction had to be measured in a sequential stopped-flow apparatus a few milliseconds after the adduct had been generated. Evidence that the observed reaction refers to the formation of $(\text{CO})_5\text{M}-\text{C}(\text{Ph})(\text{OCH}_3)_2$ ($\text{M} = \text{Cr}, \text{W}$) includes a comparison of the absorption spectrum of $(\text{CO})_5\text{W}-\text{C}(\text{Ph})(\text{OCH}_3)_2$ with that of the ylide derived from **2-W** and DABCO, low-temperature IR of the adducts, and demonstration of $\text{CH}_3\text{O}/\text{CD}_3\text{O}$ exchange on the same time scale as the kinetic experiments. The following rate and equilibrium constants were obtained: $k_1 = 77.1 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = 1.10 \text{ s}^{-1}$, and $K_1 = 70.1 \text{ M}^{-1}$ for **2-Cr** and $k_1 = 186 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1} = 1.68 \text{ s}^{-1}$, and $K_1 = 111 \text{ M}^{-1}$ for **2-W**. Approximate intrinsic rate constants ($k_0 = k_1 = k_{-1}$ when $K_1 = 1$) were calculated from the experimental rate constants. The k_0 values are substantially lower than those estimated for the addition of methoxide ion to methyl benzoate. This is consistent with significant charge delocalization in the methoxide ion adducts of the metal carbene complexes. Rate constants, k_{-1}^{BH} , for general acid catalyzed methoxide ion loss from the adducts by phenol and 3,5-dichlorophenol were also determined. They allow an estimate of a Brønsted α value on the order of 0.9, suggesting a transition state in which proton transfer from the catalyst to the incipient methoxide ion is well advanced. The near-independence of K_1 on the metal contrasts with the strong metal dependence (Cr vs W) of the $\text{p}K_{\text{a}}$ values of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$ -type hydrido complexes and supports Norton's view that the acidity of these hydrido complexes is not governed by the stabilization of the negative charge in the respective anions.

Since the first targeted synthesis of [methoxy(methyl)carbene]pentacarbonyltungsten(0) (**1-W**) by Fischer and Maasböl,³ the chemistry of transition metal carbene complexes (Fischer carbene complexes) has developed in



an almost explosive fashion and has become an important branch of organometallic chemistry.⁴ The major thrust of this development has been toward the preparation and characterization of these complexes and their use as synthons and catalysts.

This intensive activity in the area of synthesis is in sharp contrast with the modest efforts toward thorough kinetic

studies of even the simplest reactions of prototypical Fischer carbene complexes such as **1-M** and **2-M**. (Throughout this paper we shall use the symbols **1-M**, **2-M**, etc. when both the chromium and tungsten derivatives are meant.) For example, the substitution of the methoxy group in complexes such as **1-M** and **2-M** by amines,⁵ thiolate ions,⁶ carbanions,⁷ and other nucleophiles⁸ is well documented in numerous papers, yet we are aware of only one kinetic investigation outside of our laboratory, that of the reaction of **2-Cr** with primary amines in *n*-decane, dioxane, methanol, and dioxane-methanol

* Abstract published in *Advance ACS Abstracts*, April 15, 1994.

(1) Part 3: Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **1993**, *115*, 12526.

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(3) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

(4) For recent reviews, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (c) Wulff, W. D. *Adv. Met.-Org. Chem.* **1989**, *1*, 209. (d) Schubert, U., Ed. *Advances in Metal Carbene Chemistry*; Kluwer: Dordrecht, Holland, 1989. (e) Schmidt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (f) Veillard, A. *Chem. Rev.* **1991**, *91*, 743.

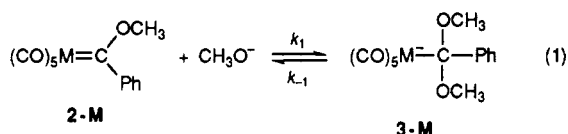
(5) (a) Reference 4a, p 153. (b) Klabunde, U.; Fischer, E. O. *J. Am. Chem. Soc.* **1967**, *89*, 7141. (c) Connor, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578. (d) Fischer, E. O.; Kollmeier, H.-J. *Chem. Ber.* **1971**, *104*, 1339. (e) Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599. (f) Fischer, E. O.; Heckl, B.; Werner, H. *J. Organomet. Chem.* **1971**, *28*, 359.

(6) (a) Fischer, E. O.; Leupold, M.; Kreiter, C. G.; Müller, J. *Chem. Ber.* **1972**, *105*, 150. (b) Lam, C. T.; Senoff, C. V.; Ward, J. E. H. *J. Organomet. Chem.* **1974**, *70*, 273. (c) Aumann, R.; Schröder, J. *Chem. Ber.* **1990**, *123*, 2053.

(1:1) mixtures reported by Werner et al.⁹ In these solvents complications arise due to the low solvent polarity which makes mechanistic interpretations difficult, particularly in *n*-decane and dioxane.¹⁰

We have recently initiated a program aimed at studying the kinetics of reactions of 1-M and 2-M and derivatives thereof with various nucleophiles in polar solvents. Our objective is to firmly establish the mechanisms of these reactions and to develop a deeper understanding of the structure-reactivity behavior in these systems. In a recently completed study¹¹ we have provided the first compelling kinetic evidence for the stepwise nature of the mechanism of aminolysis of 2-Cr in 20% acetonitrile-80% water.

In the present paper we report a kinetic study of the reversible addition of methoxide ion to 2-Cr and 2-W in methanol (eq 1). This reaction is formally analogous to



the formation of a tetrahedral intermediate in the reaction of acyl esters with CH_3O^- or the formation of a Meisenheimer complex from a nitro activated anisole and of adducts derived from electrophilic alkenes. Our work shows both similarities and differences in the kinetics and thermodynamics of eq 1 compared to these systems. This study also addresses the question of the strength of the $\text{Cr}(\text{CO})_5$ vs the $\text{W}(\text{CO})_5$ moiety in stabilizing negative charge. This question is not only relevant with respect to the adducts 3-Cr and 3-W but also with respect to the relative acidity of chromium vs tungsten hydrides, e.g., $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$ vs $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}$.¹²

Results

General Features. In methanolic sodium methoxide solution and even in neutral methanol 2-Cr and 2-W undergo a number of transformations that occur on different time scales. It is therefore important to establish which of these processes refers to eq 1. Dilute solutions ($\leq 10^{-4}$ M) of 2-Cr and 2-W in neutral methanol show significant changes in their absorption spectra within a few minutes. These changes are characterized by a red shift of the long-wavelength maximum from 398 to 438 nm for 2-Cr and from 396 to 418 nm for 2-W. Figure 1 shows these spectral changes for 2-W. Over a longer period of time the new absorptions in the visible range gradually disappear.

(7) (a) Fischer, E. O.; Riedmüller, S. *Chem. Ber.* **1976**, *109*, 3358. (b) Fischer, E. O.; Held, W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 3842. (c) Burkhardt, T. J.; Casey, C. P. *J. Am. Chem. Soc.* **1973**, *95*, 5833. (d) Fischer, E. O.; Held, F. R.; Kreissl, F. R.; Frank, A.; Hattner, G. *Chem. Ber.* **1977**, *110*, 656. (e) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

(8) (a) Fischer, E. O.; Kreis, G.; Kreissl, F. R.; Kreiter, C. G.; Müller, J. *J. Chem. Ber.* **1973**, *106*, 3910. (b) Casey, C. P.; Brunsvold, W. P. *Inorg. Chem.* **1977**, *16*, 391. (c) Bell, R. A.; Chisholm, M. H.; Couch, D. A.; Rankel, L. A. *Inorg. Chem.* **1977**, *16*, 677.

(9) Werner, H.; Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, *28*, 367.

(10) For example, in *n*-pentane the reaction is third order in the amine concentration.

(11) Bernasconi, C. F.; Stronach, M. W. *J. Am. Chem. Soc.* **1993**, *115*, 1341.

(12) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) Kristjánssdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; Verlag Chemie: New York, 1992; p 309.

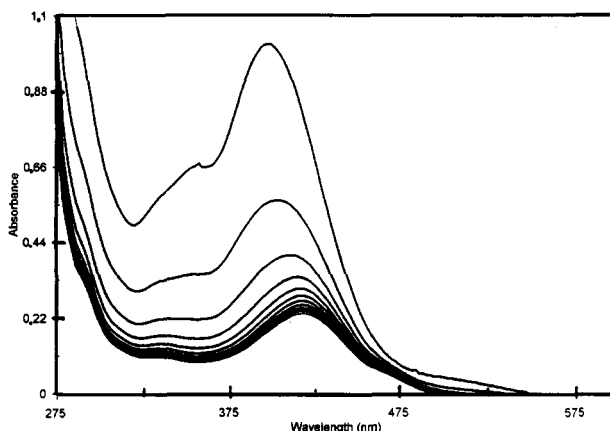
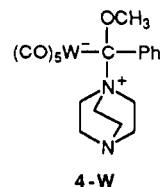


Figure 1. Repetitive UV-vis spectra showing the decay of 2-W in a 10^{-3} M NaOMe solution. Time intervals between scans are 30 s.

These transformations are accelerated in the presence of sodium methoxide and can be effectively suppressed by adding small amounts of methanesulfonic acid to the solution. This dependence on the basicity of the solution is, in principle, consistent with formation of 3-M. However, the following observations are in disagreement with such an interpretation. (1) Acidification of a neutral reaction solution after formation of the species with λ_{max} 438 (2-Cr) and 418 nm (2-W) is complete (ca. 3 min), or after a longer time, does *not* lead to recovery of the substrate. (2) Since in the formation of 3-M the chromophore responsible for the longer wavelength maximum of 2-M is destroyed, we would expect a blue shift instead of a red shift upon formation of 3-M. (3) In neutral methanol, reaction of 2-M only occurs at a significant rate if the solution is dilute ($\leq 10^{-4}$ M). At 0.05 M the solutions are quite stable over several days; in methanol-*d*₄ gradual exchange of the CH_3O group for CD_3O takes place as monitored by ^1H NMR. Since the focus of this study is on eq 1, the reactions described above were not further examined. However, it was established that, at least for the initial process leading to the red shifts, the reaction occurs at about the same rate even in carefully deoxygenated solution (see Experimental Section).

Formation of 3-M occurs on a much faster time scale than the above processes. Figure 2 shows spectra of a 10^{-4} M solution of 2-W in the presence of 0.186 M NaOMe taken 10 ms after mixing and then at subsequent time intervals of about 30 ms. The spectra were constructed from kinetic traces generated at 5-nm intervals in a stopped-flow spectrophotometer. They show the disappearance of the $d \rightarrow \pi^*$ (carbene) MLCT band,¹³ which is replaced by a much lower maximum or shoulder at ~ 370 nm. These spectral changes are very similar to those observed in the reaction of 2-W with DABCO to form the ylide 4-W (Figure 3). 4-W is a well characterized com-



pound,¹⁴ but its absorption spectrum has never been published. We have synthesized and isolated 4-W; the spectrum of the isolated sample and the one generated in

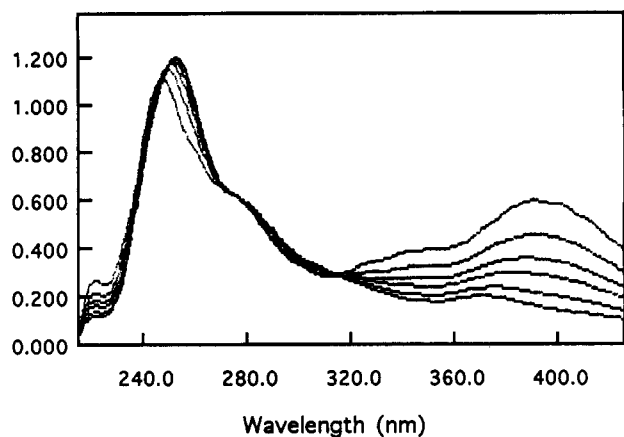


Figure 2. Repetitive UV-vis spectra showing the transformation of 2-W into 3-W in a 0.186 M NaOMe solution. Spectra were taken in the Applied Photophysics DX.17MV stopped-flow apparatus. The first scan (λ_{max} 398 nm) was made 10 ms after mixing; subsequent scans were made at ~ 30 -ms intervals.

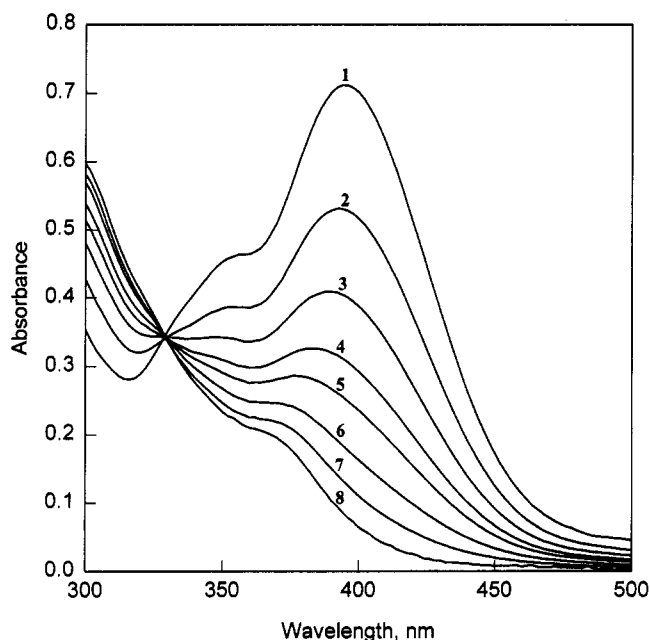


Figure 3. Repetitive UV-vis spectra showing the transformation of 2-W into 4-W in a 0.53 M DABCO solution in acetonitrile ($[2\text{-W}]_0 = 7.4 \times 10^{-5}$ M). Spectrum 1 is 2-W in the absence of DABCO; spectrum 8 is that of an isolated sample of 4-W. Spectra 2-7 were taken approximately 4, 10, 16, 22, 34, and 50 s, respectively, after mixing.

situ are indistinguishable (Figure 3). In the presence of 0.53 M DABCO in acetonitrile, the process is complete after about 120 s ($t_{1/2} \approx 12$ s).

Acidification of the solution of 3-W with a 3,5-dichlorophenol buffer within 1-2 s after formation in a sequential mixing stopped-flow apparatus leads to virtually 100% recovery of 2-W, as judged by the absorption spectrum of the resulting solution; if acidification is delayed significantly, recovery of 2-W is incomplete and for still longer delays very little if any 2-W can be recovered.

These results are consistent with the formation of 3-W, which is expected to have an absorption spectrum similar

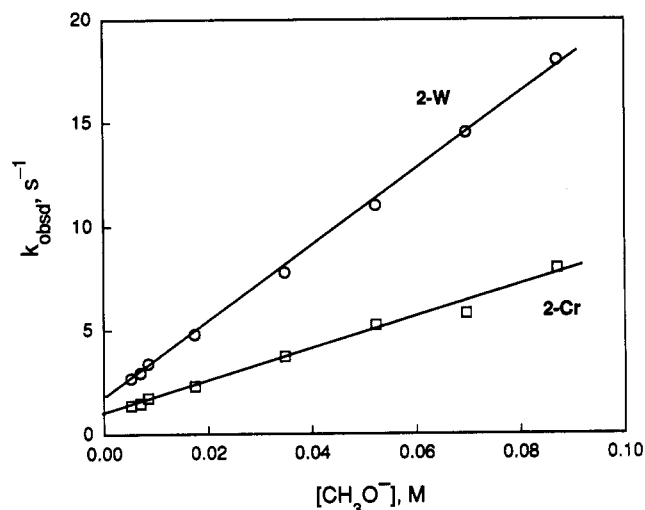


Figure 4. Kinetics of the reactions of 2-Cr and 2-W with NaOMe.

to that of 4-W. Our measurements also show that eq 1 is fully reversible on a subsecond time scale. Similar observations were made with 2-Cr, which establish the reversible formation of 3-Cr according to eq 1. Additional evidence demonstrating that the process observed on the millisecond time scale refers to reversible formation of 3-M comes from NMR and IR experiments. In the NMR experiments, a few milliliters of a concentrated NaOCD₃ solution in CD₃OD was added to a solution of 0.05 M 2-W in the same solvent, to generate a solution ca. 0.05 M in the adduct and 0.05 M in NaOCD₃. At 2.5 s after mixing, the solution was neutralized with a few drops of DCl. The ¹H NMR of this neutralized solution showed that the CH₃O signal of the original 2-W had virtually disappeared while the ¹³C NMR spectrum was indistinguishable from that of 2-W taken before the experiment. A control experiment in which a CD₃OD solution of 2-W was treated with DCl showed the absence of any methoxy group exchange.

For the IR experiments, 3-W and 3-Cr were generated in the presence of 0.4 M NaOCH₃; the temperature was kept at ca. -78 °C (dry ice-ethanol) in order to slow down the decomposition reactions. The IR taken showed substantial shifts in the C-O stretching frequencies compared to those in the carbene complexes, consistent with the formation of adducts: for 2-W \rightarrow 3-W the bands at 2069 (m), 1981 (s), and 1940 cm⁻¹ (vs) were replaced by bands at 2042 (m), 1900 (s), and 1848 cm⁻¹ (w), respectively, while for 2-Cr \rightarrow 3-Cr the bands at 2061 (m), 1985 (w), and 1949 cm⁻¹ (vs) were replaced by bands at 2042 (m), 1901 (s), and 1857 cm⁻¹ (m), respectively.¹⁵ After neutralization of the adduct solutions with *p*-toluenesulfonic acid, the IR spectra showed that 2-W and 2-Cr had been regenerated.

Kinetics. Two types of experiments were performed. In the first, reaction was initiated by mixing 2-M with a NaOMe solution in a stopped-flow apparatus. NaOMe was always in large excess, ensuring pseudo-first-order conditions. The raw data are summarized in Table S1 of the supplementary material.¹⁶ Plots of the observed first-order rate constants vs [NaOMe] are shown in Figure 4.

(15) The frequencies of 2-W and 2-Cr are very similar to those reported by Kreissl and Fischer.¹⁴

(16) See the paragraph concerning supplementary material at the end of this paper.

(13) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* 1971, 28, 237.

(14) Kreissl, F. R.; Fischer, E. O. *Chem. Ber.* 1974, 107, 183.

Table 1. Rate and Equilibrium Constants for the Reversible Addition of Methoxide Ion to 2-Cr and 2-W in Methanol at 25 °C^a

param	2-Cr	2-W
$k_1, \text{M}^{-1} \text{s}^{-1}$	77.1 ± 3.4	186 ± 2.5
k_{-1}, s^{-1} (eq 2)	0.98 ± 0.28	1.60 ± 0.21
k_{-1}, s^{-1} (eq 3)	1.21 ± 0.05	1.76 ± 0.28
k_{-1}, s^{-1} (av)	1.10	1.68
$K_1 = k_1/k_{-1}, \text{M}^{-1}$	70.1^d	111^d
$k_{-1}^{\text{BH}}, \text{M}^{-1} \text{s}^{-1}$ ($\text{C}_6\text{H}_5\text{OH}$) ^b	9.43 ± 0.27	16.8 ± 0.5
$k_{-1}^{\text{BH}}, \text{M}^{-1} \text{s}^{-1}$ ($3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{OH}$) ^c	772 ± 15	1500 ± 29
$\log k_0^e$	0.96	1.25

^a Error limits given are standard deviations. ^b $\text{p}K_{\text{a}}^{\text{BH}} = 14.2$ for $\text{C}_6\text{H}_5\text{OH}$: Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. *J. J. Am. Chem. Soc.* **1966**, *88*, 1911. ^c $\text{p}K_{\text{a}}^{\text{BH}} = 12.1$ for $3,5\text{-Cl}_2\text{C}_6\text{H}_3\text{OH}$: Rochester, C. H.; Wilson, D. N. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2930. ^d For k_{-1} the average value is used. ^e Estimated as $\log k_0 = \log k_{-1} - 0.5 \log K_1$; see text.

They yield k_1 from the slope and k_{-1} from the intercept (Table 1) according to eq 2.

$$k_{\text{obsd}} = k_1[\text{MeO}^-] + k_{-1} \quad (2)$$

Further evidence for a reversible addition reaction such as eq 1 comes from the dependence of the reaction amplitudes (changes in absorbance caused by the reaction) on $[\text{MeO}^-]$. For $K_1[\text{MeO}^-] \gg 1$ ($K_1 = k_1/k_{-1}$), which means that **3-M** is strongly favored over **2-M**, the amplitudes are large and independent of $[\text{MeO}^-]$. At lower $[\text{MeO}^-]$, where $K_1[\text{MeO}^-]$ is no longer $\gg 1$, the amplitudes become smaller. In fact, the concentration dependence of the amplitudes allowed a determination of K_1 for **2-W**, as described in the Experimental Section. The K_1 value of $127 \pm 16 \text{ M}^{-1}$ obtained by this method is in good agreement with $K_1 = k_1/k_{-1} = 111 \pm 15 \text{ M}^{-1}$ determined kinetically. For the reaction of **2-Cr** a quantitation of the amplitudes at low $[\text{MeO}^-]$ was more difficult because of significant interference by the decomposition reaction of **2-Cr**; however, the qualitative trend toward lower amplitudes at low $[\text{MeO}^-]$ was clearly evident for this reaction as well.

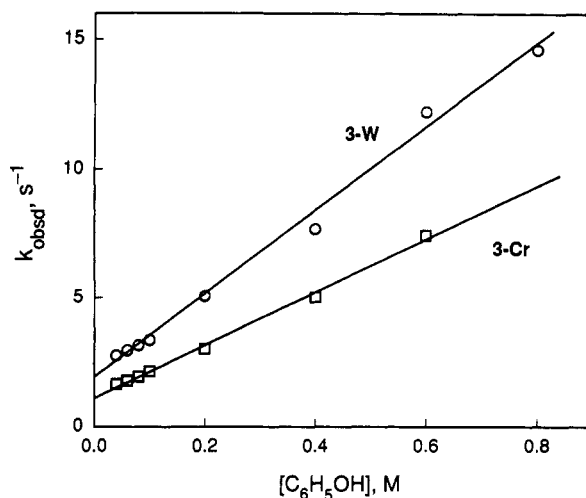
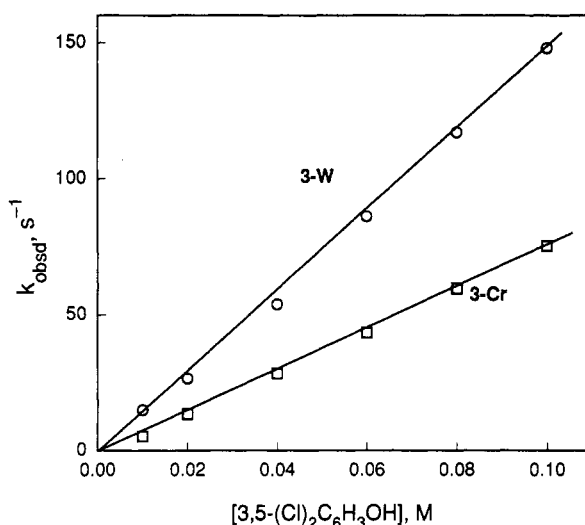
The second type of kinetic experiment involved generation of **3-M** in the presence of 0.1 M NaOMe and subsequent addition of phenol and 3,5-dichlorophenol buffers. Since **3-M** is quite unstable, addition of the buffer had to occur in a sequential mixing stopped-flow apparatus within 1–2 s after generation of the adduct. This led to quantitative recovery of **2-M**, with a pseudo-first-order rate constant given by eq 3, in which k_{-1}^{BH} refers to the

$$k_{\text{obsd}} = k_{-1}^{\text{BH}}[\text{BH}] + k_{-1} \quad (3)$$

buffer acid catalyzed loss of methoxide ion from **3-M**. Plots of k_{obsd} vs $[\text{BH}]$ are shown in Figures 5 and 6, while the k_{-1}^{BH} and k_{-1} values are summarized in Table 1. With 3,5-dichlorophenol, catalysis was very strong (high $k_{-1}^{\text{BH}}/k_{-1}$ ratio) and hence the intercepts (k_{-1}) were indistinguishable from zero. Catalysis was much weaker with phenol, which allowed the determination of k_{-1} ; these k_{-1} values are very close to those determined from eq 2, indicating internal consistency of our data.

Discussion

Evidence for the Reversible Formation of 3-M on a Millisecond Time Scale. The quantitative recovery of **2-M** upon acidification of **3-M** within about 2 s after **3-M** was generated shows that the reaction is reversible

**Figure 5.** Kinetics of the reactions of **3-Cr** and **3-W** with phenol.**Figure 6.** Kinetics of the reactions of **3-Cr** and **3-W** with 3,5-dichlorophenol.

under conditions where irreversible decomposition occurs on a longer time scale. The kinetic behavior, including the $[\text{MeO}^-]$ dependence of the amplitudes, also demonstrates reversibility.

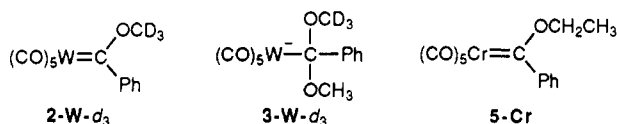
There are three pieces of evidence that support our assignment of the observed reversible process to eq 1.

The first is the strong similarity of the UV spectrum of the adduct (Figure 2) with that of the ylide **4-W** (Figure 3).

The second is that the IR frequencies of the strongest absorption of the adducts (1900 cm^{-1} for **3-W** and 1901 cm^{-1} for **3-Cr**) are comparable to those observed for **4-W** (1898 cm^{-1})¹⁴ or upon ylide formation between **1-Cr** and phosphines ($1902\text{--}1908 \text{ cm}^{-1}$).¹⁷ The fact that **2-W** and **2-Cr** are regenerated upon neutralization of the solution demonstrates that the observed species must be **3-W** and **3-Cr**, respectively, rather than decomposition products. It should be noted, though, that the IR data were obtained at a much lower temperature than the kinetic data. Hence, strictly speaking, they only indicate that **3-M** is formed at low temperature, leaving open the possibility for a different reaction at room temperature.

(17) Fischer, H.; Fischer, E. O.; Kreiter, C. G.; Werner, H. *Chem. Ber.* **1974**, *107*, 2459.

The third and most compelling evidence is the exchange of the CH_3O for a CD_3O group on the same time scale as the kinetically monitored reaction, to form **2-W-d₃**. The



strength of this piece of evidence derives from the fact that the exchange experiments were performed under conditions (temperature, solvent) that were the same as those in the kinetic experiments. The exchange of the CH_3O group also excludes the possibility that the observed reaction represents a nucleophilic attack on a CO ligand.¹⁸ Under the conditions of the exchange experiment ($[\text{CD}_3\text{O}^-] \approx 0.05 \text{ M}$), we have $K_1[\text{CD}_3\text{O}^-] \approx 5.5$; i.e., the equilibrium strongly favors adduct formation. Thus, the rate-limiting step for the exchange is the expulsion of CH_3O^- from **3-W-d₃**, which has the statistically corrected rate constant $0.5k_{-1} = 0.84 \text{ s}^{-1}$. This corresponds to a half-life of about 0.8 s and implies approximately 88% exchange within the 2.5-s duration of the experiment, consistent with the almost complete disappearance of the CH_3O^- ^1H NMR signal.

We have also observed, by ^1H NMR, slow formation of **2-W-d₃** in CD_3OD in the absence of base, and Schubert and Fischer²¹ have reported similar observations in the presence of catalytic amounts of NaOCD_3 . However, even though these observations, as well as Kreiter's²² report of the conversion of **5-Cr** into **2-Cr** in methanolic NaOMe , are consistent with eq 1, they do not demonstrate that eq 1 corresponds to our fast kinetic process. It is only the fast time scale NMR exchange experiment that provides this evidence. This point is important because of the various decomposition reactions that occur on a slower time scale in basic methanolic solutions of **2-M**.

Regarding these slower processes, they were not the focus of the present study and speculation about their nature would be inappropriate without further examination. It is likely, though, that some of the products formed are the same as those observed by Fischer et al.²³ under similar reaction conditions and traced to **3-M** as precursor. As indicated under Results, rigorous removal of oxygen had little effect, suggesting that at least the initial slow process does not involve oxygen. Nevertheless, the fact that the solutions were much more stable at high substrate concentrations could be consistent with an oxygen-dependent reaction; at high concentration the remaining traces of oxygen would presumably be scavenged by reacting with just a small fraction of the carbene complex, but at low concentration most of the carbene complex could be consumed by reaction with oxygen.

Rate and Equilibrium Constants. Turning to the rate and equilibrium data summarized in Table 1, we note the striking similarity between **2-Cr** and **2-W** with respect to these parameters. The equilibrium constants differ by

(18) This possibility is quite remote in view of numerous experimental¹⁴⁻⁹ as well as theoretical studies^{19,20} that show the carbene carbon to be the generally preferred site of attack by nucleophiles, but it has been suggested by a reviewer.

(19) Block, T. F.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* 1976, 98, 441.

(20) Kostić, N. M.; Fenske, R. F. *Organometallics* 1982, 1, 974.

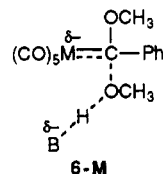
(21) Schubert, U.; Fischer, E. O. *Justus Liebig's Ann. Chem.* 1975, 393.

(22) Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* 1968, 7, 390.

(23) Fischer, E. O.; Schubert, U.; Kalbfus, W.; Kreiter, C. G. *Z. Anorg. Allg. Chem.* 1975, 416, 135.

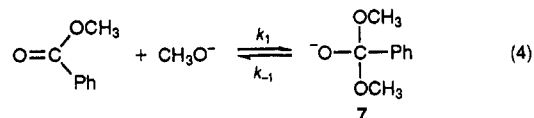
less than 2-fold, while the rate constants k_1 , k_{-1} , and k_{-1}^{BH} are somewhat larger for the tungsten complex. The higher rate constants indicate that the intrinsic rate constant, k_0 ,²⁴ is slightly higher for the reaction of **2-W** or the intrinsic barrier, ΔG_0^\ddagger ,²⁴ is slightly lower. k_0 values estimated as $\log k_0 = \log k_1 - 0.5 \log K_1$ ²⁷ are included in Table 1; they differ by less than a factor of 2 between **2-Cr** and **2-W**, which is too small a difference to warrant attempts at a detailed interpretation.

The rate constants k_{-1}^{BH} for phenol- and 3,5-dichlorophenol-catalyzed methoxide ion departure from **3-M** most likely refer to a concerted process with the transition state **6-M**.²⁹ From a two-point Brønsted plot of $\log k_{-1}^{\text{BH}}$



vs $-\text{p}K_a^{\text{BH}}$, approximate α values can be obtained. They are 0.91 for **3-Cr** and 0.93 for **3-W**, suggesting a transition state in which proton transfer from BH to the departing methoxide ion is far advanced.

Comparison of 2-M with Other Electrophiles. It is instructive to compare the kinetic and thermodynamic parameters of eq 1 with those for the reaction of CH_3O^- with other electrophiles. A summary of the relevant parameters is given in Table 2. Fischer carbene complexes have frequently been compared with acyl esters.^{4a,d} The ester analogue of eq 1 is the formation of the tetrahedral intermediate **7**, as shown in eq 4. **7** cannot be observed



in methanol solution, because the equilibrium (K_1) of eq 4 is very unfavorable. An approximate K_1 value between 10^{-7} and $5 \times 10^{-7} \text{ M}^{-1}$ may be estimated,³² suggesting that formation of **3-M** is (2×10^8)- to 10^9 -fold more favorable than **7**; i.e., the $(\text{CO})_5\text{M}$ moiety is much more effective in stabilizing negative charge than oxygen. This can, at least in part, be attributed to a resonance effect brought about by delocalization of the negative charge into the CO ligands

(24) For a reaction with forward and reverse rate constants k_1 and k_{-1} , k_0 is defined as $k_0 = k_1 = k_{-1}$ when $K_1 = 1$ and ΔG_0^\ddagger is defined as $\Delta G_1^\ddagger = \Delta G_{-1}^\ddagger$ when $\Delta G^\circ = 0$. For a reaction such as eq 1 where the molecularities in the two directions are different, these definitions are somewhat problematic because k_1 and k_{-1} have different units. Hine²⁶ has suggested a possible remedy but one that creates its own problems, as discussed elsewhere.²⁸ As long as the k_0 or ΔG_0^\ddagger values defined above are only used for comparisons between systems of the same type, as is the case in the present study, the different molecularities are inconsequential.

(25) Hine, J.; Weimar, R. D., Jr. *J. Am. Chem. Soc.* 1965, 87, 3387.

(26) Bernasconi, C. F. *Adv. Phys. Org. Chem.* 1992, 27, 119.

(27) This is equivalent to applying the simplest version of the Marcus equation,²⁸ $\Delta G^\ddagger = \Delta G_0^\ddagger + 0.5\Delta G^\circ + (\Delta G^\circ)^2/16\Delta G_0^\ddagger$, and neglecting the third term, which is very small in our case.

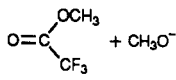
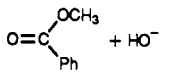
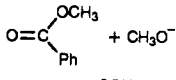
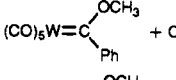
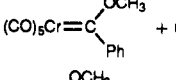
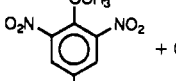
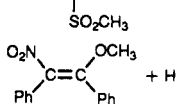
(28) Marcus, R. A. *J. Chem. Phys.* 1965, 43, 679.

(29) According to the Jencks³⁰ classification, this is a class *n* mechanism. It is customary to use the term "catalysis" for such processes,^{30,31} even though the phenols are converted to aryloxide ions and are not regenerated, as pointed out by a reviewer.

(30) Jencks, W. P. *Acc. Chem. Res.* 1976, 9, 425.

(31) (a) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969. (b) Bunnett, J. F. In *Investigation of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley-Interscience: New York, 1986; Part I, p 251.

Table 2. Equilibrium Constants, Rate Constants, and Intrinsic Rate Constants for Reactions of Electrophiles with Methoxide or Hydroxide Ion

reacn	$k_1, \text{M}^{-1} \text{s}^{-1}$	K_1, M^{-1}	approx log k_0^a	ref
	3.5×10^3	7.0	3.10	44
	0.072	$\sim 8.3 \times 10^{-8}$	2.4	35, 37
		$> 1.1 \times 10^{-7}, ^b \sim 5.0 \times 10^{-7c}$	3.10^d	
	186	111	1.25	this work
	77.1	70.1	0.96	this work
	1.75	101	-0.76	47
	0.69^e	$\geq 3.8 \times 10^7^e$	-3.9^e	48

^a Estimated as $\log k_0 = \log k_1 - 0.5 \log K_1$. ^b Estimated on the basis of eq 5; see text. ^c Estimated on the basis of eq 6 and by assuming a ~ 6 -fold increase for the change from $\text{OH}^-/\text{H}_2\text{O}$ to $\text{CH}_3\text{O}^-/\text{CH}_3\text{OH}$; see text. ^d Assumed to be the same as for eq 5; see text. ^e In 50% Me_2SO -50% water at 20 °C.

of 3-M. A similar manifestation of the greater effectiveness in stabilizing the negative charge is seen when comparing the acidity of 1-Cr ($\text{p}K_a = 12.3$)³⁹ to that of methylacetate ($\text{p}K_a = 24.5$).⁴⁰

Independent evidence for such charge delocalization comes from our IR data and those of others. The CO stretching frequency shifts on the order of 80–90 cm^{-1} observed upon conversion of 2-M to 3-M indicate a reduction in the C=O double-bond character of the CO ligands. Even larger shifts ($> 100 \text{ cm}^{-1}$) occur when hydrido complexes such as $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$ are deprotonated.^{12a}

The above evidence clearly establishes the importance of charge delocalization, but it does not provide a quantitative assessment of how much the resonance effect contributes to the enhanced thermodynamic driving force of eq 1 compared to eq 4. Other factors that are likely to contribute include differences in inductive effects between the $(\text{CO})_5\text{M}$ moiety and the carbonyl oxygen in the ester, differences in the strengths of C=O vs C=M double bonds that need to be broken, and also resonance effects in the substrates.

(32) One estimate is based on $K = 2.2 \times 10^{-12} \text{ M}^{-1}$ for $\text{PhCOOMe} + \text{MeOH} \rightleftharpoons \text{PhC}(\text{OMe})_2\text{OH}$ in 50% aqueous dioxane,³⁸ from which K_1 for eq 4 is obtained as $K[K_a(\text{PhC}(\text{OMe})_2\text{OH})]/K_a(\text{MeOH})$. Using $\text{p}K_a(\text{PhC}(\text{OMe})_2\text{OH}) \approx 11.0$ ³⁸ and $\text{p}K_a(\text{MeOH}) \approx 15.7$ ³⁴ yields $K_1 \approx 1.1 \times 10^{-7} \text{ M}^{-1}$ in 50% aqueous dioxane. In methanol K_1 may be somewhat higher. A similar K_1 value is obtained on the basis of Guthrie's estimate of $8.3 \times 10^{-8} \text{ M}^{-1}$ for the equilibrium constant of $\text{PhCOOMe} + \text{OH}^- \rightleftharpoons \text{PhC}(\text{OMe})(\text{OH})\text{O}^-$ in water.³⁷ Assuming K_1 for MeO addition in methanol (eq 1) is about 6-fold larger,³⁸ one obtains $K_1 \approx 5 \times 10^{-7} \text{ M}^{-1}$.

(33) McClelland, R. A.; Patel, G. *J. Am. Chem. Soc.* 1981, 103, 6912.

(34) $\text{p}K_a(\text{MeOH}) = 15.49$ in water.³⁶ In 50% aqueous dioxane it is assumed that the $\text{p}K_a$ of methanol increases by the same amount as the $\text{p}K_a$ of water, i.e., by 0.2 unit based on an increase in $\text{p}K_w$ of 0.5.³⁶

(35) Guthrie, J. P. *Can. J. Chem.* 1978, 56, 2342.

(36) McClelland, R. A.; Patel, G. *J. Am. Chem. Soc.* 1981, 103, 6908.

(37) Guthrie, J. P.; Cullimore, P. A. *Can. J. Chem.* 1980, 58, 1281.

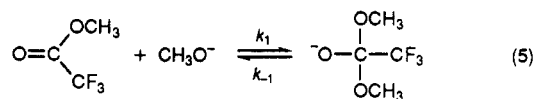
(38) The equilibrium constant for MeO⁻ addition to 1,3,5-trinitrobenzene in methanol is 6.2-fold larger than for OH⁻ addition in water: Bernasconi, C. F. *J. Am. Chem. Soc.* 1970, 92, 4682.

(39) Gandler, J. R.; Bernasconi, C. F. *Organometallics* 1989, 8, 2282.

(40) Streitwieser, A.; Heathcock, C. H. *Introduction to Organic Chemistry*; Macmillan: New York, 1985, p 1156.

Some insight into the relative importance of the resonance effect may be obtained by comparing the estimated intrinsic rate constants (k_0) for eq 1 with estimates for k_0 for eq 4. It is well-known that the intrinsic rate constants of reactions that lead to resonance-stabilized products or involve loss of resonance in a reactant are generally lower than those for comparable reactions where resonance plays a lesser role.⁴¹ This phenomenon has been attributed to the greater electronic/structural/solvational reorganization that takes place in such reactions and enhances the barrier;⁴² more specifically it appears to be the lag of this reorganization behind bond changes and/or charge transfer at the transition state which creates the additional barrier.^{26,43}

Since no relevant data are available that would permit the calculation of k_0 for eq 4, we need to rely on models. One such model is eq 5, for which $k_1 = 3.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$



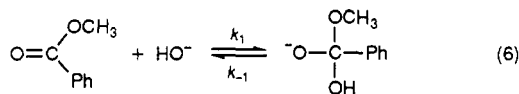
and $K_1 = 7.0 \text{ M}^{-1}$,⁴⁴ hence, $\log k_0 \approx \log k_1 - 0.5 \log K_1 = 3.10$. An alternative model is eq 6. From the rate constant for OH⁻ addition ($k_1 = 0.072 \text{ M}^{-1} \text{ s}^{-1}$)³⁷ and the estimated $K_1 \approx 8.3 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$,³⁵ $\log k_0 \approx 2.4$ can be estimated. Inasmuch as a somewhat higher k_0 is expected for methoxide ion addition in methanol than for hydroxide ion addition in water,⁴⁵ this alternative model yields a k_0

(41) For a recent review, see ref 26.

(42) (a) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; Chapter 10. (b) Ritchie, C. D. In *Solute-Solvent Interactions*; Coetzee, J. F., Ritchie, C. D., Eds.; Dekker: New York, 1969; p 219. (c) Kresge, A. J. *Acc. Chem. Res.* 1975, 8, 354. (d) Hibbert, F. *Compr. Chem. Kinet.* 1977, 8, 97. (e) Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic Press: New York, 1985.

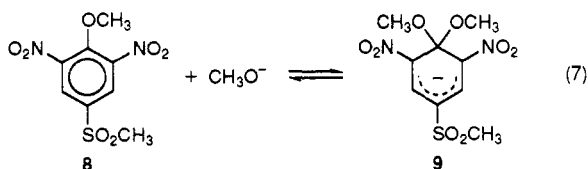
(43) (a) Bernasconi, C. F. *Acc. Chem. Res.* 1987, 20, 301. (b) Bernasconi, C. F. *Tetrahedron* 1989, 45, 4017. (c) Bernasconi, C. F. *Acc. Chem. Res.* 1992, 25, 9.

(44) Guthrie, J. P. *Can. J. Chem.* 1976, 54, 202.



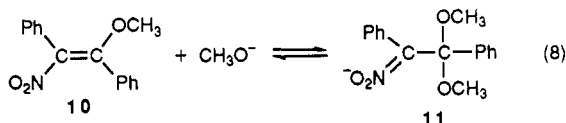
value that is consistent with that estimated for eq 5. For the sake of discussion we shall therefore adopt $\log k_0 \approx 3.1$ for eq 4.

It is clear that the $\log k_0$ values for methoxide ion addition to the carbene complexes (0.93 for 2-Cr and 1.24 for 2-W) are significantly lower than for the addition to methyl benzoate. However, the lowering of k_0 by approximately 2 log units is hardly dramatic if compared with k_0 values for reactions of other electrophiles with methoxide ion. For example, $\log k_0 \approx -0.77$ may be estimated for the Meisenheimer complex formation in methanol shown in eq 7.⁴⁷ The roughly 100-fold lower k_0



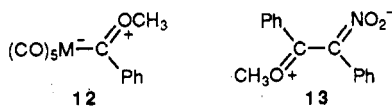
for eq 7 suggests that the resonance component in the stabilization of 9 must be significantly larger than that in the stabilization of 3-M.

A more relevant example is eq 8, which is directly comparable with eqs 1 and 4. Using the reaction of OH^- with β -methoxy- α -nitrostilbene (10) in 50% aqueous Me_2SO as a model ($k_1 = 0.69 \text{ M}^{-1} \text{ s}^{-1}$, $K_1 \geq 3.8 \times 10^7 \text{ M}^{-1}$)⁴⁸ affords $\log k_0 \approx -3.9$. Even if k_0 is somewhat higher for



CH_3O^- in methanol,⁴⁵ it is several orders of magnitude below that for eq 1, indicating a much stronger resonance effect in the stabilization of 11 compared to 3-M. If we assume that the lowering of $\log k_0$ is roughly inversely proportional to the degree of resonance stabilization of the product,⁴⁹ the rather modest decrease in $\log k_0$ for eq 1 compared to eq 4 suggests that only a relatively small fraction of the extra stability of 3-M is due to resonance.

It is possible that the resonance effect caused by charge delocalization into the CO ligands is not the only factor that lowers k_0 . There is extensive evidence that indicates 12 to be an important resonance structure of 2-M, perhaps



more important than 2-M.^{4a,50} The loss of this resonance

stabilization in converting 2-M to 3-M may contribute to the lowering of k_0 . The lower k_0 for nucleophilic additions to β -methoxy- α -nitrostilbene (10) compared with that for α -nitrostilbene is believed to be partially caused by the importance of resonance structure 13.⁵¹

Comparison with Hydrido Complexes. The very small dependence of k_1 , k_{-1} , and K_1 on the metal is interesting in light of acidity data for metal hydrido complexes of the type $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$. According to Jordan and Norton,^{12a} the $\text{p}K_a$ values are 13.3 with $\text{M} = \text{Cr}$ and 16.1 with $\text{M} = \text{W}$ in acetonitrile; in methanol, these $\text{p}K_a$ values are 6.4 and 9.0, respectively.^{12b} Norton has argued that the higher acidity of the chromium hydride is not due to more effective stabilization of the negative charge by the $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3$ moiety compared to the $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3$ moiety but can be traced to a smaller metal-H bond dissociation enthalpy of the Cr-H compared to the W-H bond.^{12b} The fact that the differences in CO stretching frequencies between the metal hydrides and their corresponding anions are very similar for the two metals^{12a} is consistent with the notion that the degree of charge delocalization is about the same for both anions. Our finding that $K_1(2\text{-Cr})$ and $K_1(2\text{-W})$ are approximately the same implies that in 3-Cr and 3-W charge stabilization is also about the same, in support of Norton's view.

Conclusions

We have demonstrated that direct detection of 3-Cr and 3-W is possible in a stopped-flow spectrophotometer and that acid-catalyzed conversion of 3-M to 2-M is quantitative if induced no later than 1–2 s after formation.

The equilibrium constants for formation of 3-M are more than 8 orders of magnitude higher than for the formation of the tetrahedral intermediate in the reaction of methyl benzoate with CH_3O^- , indicating that the $\text{M}(\text{CO})_5$ moiety stabilizes the negative charge much more effectively than oxygen. The intrinsic rate constants for the formation of 3-M are about 2 orders of magnitude lower than for the ester reaction. This finding is consistent with charge delocalization in 3-M being partially responsible for the stronger stabilization by the $\text{M}(\text{CO})_5$ moiety. However, the contribution of this resonance effect to the stabilization of 3-M is substantially smaller than the resonance in the Meisenheimer complex formed by reaction of CH_3O^- with a nitro/methylsulfonyl-activated anisole or in the adduct formed by reaction of CH_3O^- with a nitro-activated methoxystilbene.

The rate and equilibrium constants for eq 1 depend very little on the metal. The fact that the K_1 values for 2-W and 2-Cr are so similar contrasts with the much higher acidity of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$ compared to $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}$ and indicates that the stabilization of the negative charge is not the determining factor in the relative acidities of the above metal hydrides.

Experimental Section

¹H NMR spectra were recorded on a Bruker 250-MHz instrument and ¹³C NMR spectra on a GE 300-MHz or Bruker 250-MHz spectrometer. Kinetic experiments were carried out on an Applied Photophysics DX.17MV or Durrum-Gibson stopped-flow spectrophotometer. UV-vis spectra were obtained on a Perkin-Elmer Lambda 2 or Hewlett-Packard 8562 diode

(51) Bernasconi, C. F.; Fassberg, J.; Killion, R. B.; Rappoport, Z. *J. Am. Chem. Soc.* 1989, 111, 6862; 1990, 112, 3169.

(45) This expectation is based on the assumption that the partial desolvation of CH_3O^- required for the reaction to occur is less costly than the partial desolvation of HO^- . Such reduced desolvation energy typically leads to higher intrinsic rate constants.^{26,46}

(46) Jencks, W. P.; Brant, S. R.; Gandler, J. R.; Fendrich, G.; Nakamura, C. *J. Am. Chem. Soc.* 1982, 104, 7045.

(47) Terrier, F.; Millot, F.; Morel, J. *J. Org. Chem.* 1976, 41, 3892.

(48) Bernasconi, C. F.; Fassberg, J.; Killion, R. B.; Schuck, D. F.; Rappoport, Z. *J. Am. Chem. Soc.* 1991, 113, 4937.

(49) Such approximate inverse proportionality has been established for a variety of carbanion-forming reactions, including deprotonation of carbon acids, nucleophilic addition to electrophilic alkenes, and others.^{26,43}

(50) Schubert, U. *Coord. Chem. Rev.* 1984, 55, 261.

Table 3. Determination of K_1 for the Reaction of 2-W with CH_3O^- from Amplitude Measurements in Methanol at 25 °C

$10^2[\text{CH}_3\text{O}^-],$ M	$A_0 -$ A_∞	$K_1,$ M^{-1}	$10^2[\text{CH}_3\text{O}^-],$ M	$A_0 -$ A_∞	$K_1,$ M^{-1}
0.538	0.270 ^a	146	1.52	0.450 ^b	137
0.736	0.340 ^b	136	2.57	0.510 ^b	125
0.832	0.355 ^a	126	2.89	0.506 ^a	108
1.38	0.502 ^c	130	3.88	0.550 ^b	117
1.42	0.423 ^a	121			127 ± 16 ^d

^a $[\text{S}]_0 = 4.00 \times 10^{-5}$ M. ^b $[\text{S}]_0 = 4.16 \times 10^{-5}$ M. ^c $[\text{S}]_0 = 4.68 \times 10^{-5}$ M. ^d Average value.

array spectrophotometer. IR spectra were taken in a flow-through NaCl IR cell on a Perkin-Elmer 1605 FT-IR spectrometer.

Materials. Methanol was purified by fractional distillation and stored over 4-Å molecular sieves. The acetonitrile used was reagent grade and was also stored over 4-Å molecular sieves. To remove most of the oxygen in solution, argon was bubbled through the solvents for ca. 30 min before preparing substrate and base solutions. More rigorous degassing using three cycles of freezing with liquid nitrogen and thawing under vacuum did not improve the stability of dilute solutions of 2-M. Both [methoxy(phenyl)carbene]pentacarbonylchromium(0) and [methoxy(phenyl)carbene]pentacarbonyltungsten(0) were synthesized by the procedure of Lam et al.⁵² mp 48–49 °C (lit.⁵³ mp 46 °C) for 2-Cr; mp 57–59 °C (lit.⁵³ mp 59 °C) for 2-W. The ylide 4-W was prepared as described by Kreissl and Fischer,¹⁴ using sublimated 1,4-diazabicyclo[2.2.2]octane (DABCO): mp 130 °C dec (lit.¹⁴ mp 115 °C dec⁵⁴) ¹H NMR (250 MHz, acetone-*d*₆) δ 3.31 (s, 3H, OCH₃), 3.34 (m, 6, NCH₂CH₂), 3.65 (m, 6, NCH₂), 7.47 (m, 5, Ph); ¹³C NMR (62.5 MHz, acetone-*d*₆) δ 45.04 (NCH₂CH₂), 51.20 (OCH₃), 54.11 (NCH₂), 125.66, 127.19, 127.81, and 156.78 (Ph), 203.82 and 207.80 (CO); IR 2050 (m), 1949 (m), 1901 (vs) cm⁻¹. Solutions of sodium methoxide in methanol were prepared by adding freshly cut sodium metal to methanol at 0 °C and allowing the reaction to go to completion under nitrogen or argon. The concentrations of the sodium methoxide stock solutions were determined by titration against 0.10 or 1.0 M HCl using phenolphthalein as an indicator. Phenol was recrystallized from toluene; 3,5-dichlorophenol (Aldrich) was used without further purification.

Stopped-Flow Spectra and Kinetics. Kinetics were carried out by following, spectrophotometrically, the disappearance of the substrate at 396 nm in an Applied Photophysics DX.17MV stopped-flow apparatus. Stock solutions of the substrates were initially prepared in acetonitrile solution and then diluted with a methanol solution that was (2.0–4.0) × 10⁻³ M in methanesulfonic acid. The substrates were stable in these acidic solutions but decomposed in neutral solution with a half-life of ca. 3 min.

For the stopped-flow experiments in the sequential mixing mode the adduct was generated by mixing the substrate with a 0.1 M NaOMe solution. After a time delay of 2 s this solution was mixed with the solution containing the buffer acid. The buffer acid concentration was such as to both fully neutralize the MeO⁻ and to leave enough free buffer acid to produce the concentrations given in Table S2. The kinetics were monitored by following the appearance of the carbene complex (396 nm).

The spectra shown in Figure 2 were obtained from kinetic traces taken at 5-nm intervals in an Applied Photophysics DX.17MV stopped-flow apparatus.

(52) Lam, C. T.; Malkiewicz, C. D.; Senoff, C. V. *Inorg. Synth.* 1978, 17, 95.

(53) Fischer, E. O.; Maasböl, A. *Chem. Ber.* 1967, 100, 2445.

(54) Kreissl and Fischer¹⁴ did not recrystallize their ylide, which may account for their lower melting point.

Equilibrium Constants. An equilibrium constant for the addition of methoxide ion to 2-W was determined from amplitude measurements by using the equilibrium expression $K = [\text{T}^-]/[\text{S}][\text{CH}_3\text{O}^-]$, where $[\text{T}^-]$ and $[\text{S}]$ are the equilibrium concentrations of the anionic intermediate and the substrate, respectively. The concentration of substrate at equilibrium was determined from eq 9, where A_0 , A_∞ , $[\text{S}]_0$, ϵ_T , and ϵ_S are the initial and final

$$[\text{S}] = \frac{1}{2}(A_0 - A_\infty)/(\epsilon_T - \epsilon_S) - [\text{S}]_0(\epsilon_S - \epsilon_T)/(\epsilon_T - \epsilon_S) \quad (9)$$

absorbance values (at the end of the reaction), the initial substrate concentration, and the molar absorptivity constants (at 396 nm) of the intermediate (1.07 × 10³) and substrate (9.45 × 10³), respectively. The concentration of T⁻ was calculated from $[\text{T}^-] = [\text{S}]_0 - [\text{S}]$. The molar absorptivity constant of the substrate was determined in a mock stopped-flow run in the absence of base, whereas the constant for the intermediate was determined at high methoxide ion concentration, conditions under which virtually all the substrate is in the form of the intermediate. The results are summarized in Table 3.

¹H NMR. The ¹H NMR spectrum of a 0.050 M solution of 2-W in CD₃OD shows a singlet at δ 4.74 (3H) and a multiplet centered at δ 7.42 (5H). These chemical shifts are virtually identical with the shifts observed for the compound in CDCl₃ (δ 4.77 (s, 3H) and 7.40 (m, 5H)) or in acetone-*d*₆ (δ 4.72 and 7.41).¹³ Over a period of several days in CD₃OD, the peak at δ 4.74 disappears and a new one arises at δ 3.29 (s, 3H). These spectral changes are consistent with exchange of a CD₃O⁻ group from the solvent for the CH₃O⁻ group of the substrate, with the formation of 1 equiv of CH₃OD (δ 3.29 (s, 3H)). Similar observations were made after generating 2-W-*d*₃ in basic CD₃OD and quenching it with DCl 2.5 s later.

¹³C NMR. The ¹³C NMR spectra of 2-W and 2-W-*d*₃ in CD₃OD show signals at δ 323.84 (carbene carbon), 204.81 and 198.39 (CO), 156.76, 132.90, 129.22, and 127.23 (phenyl), and 71.50 (CH₃O). In CHCl₃ Bodner et al.⁵⁵ report δ 321.82 (carbene carbon), 203.60 and 197.22 (CO), and 69.86 (CH₃O).

IR Experiments. A stock solution of 2-M in *n*-hexane (30 μL, ~0.02 M) was added to 0.3 mL of a 0.4 M NaOCH₃ solution in methanol at dry-ice-ethanol bath temperature. As soon as the dark orange-red color had faded to a pale yellow (ca. 5 s), the reaction solution was diluted with an equal volume of acetonitrile⁵⁶ and the IR spectrum taken. The IR cell was not thermostated, and hence, the temperature during the IR measurements (4–16 s) rose substantially above -78 °C. However, the fact that 2-M could be regenerated after neutralization with *p*-toluenesulfonic acid demonstrates that the increase in temperature was insufficient to lead to significant decomposition.

Acknowledgment. This research was supported by Grants CHE-8921739 and CHE-9307659 from the National Science Foundation.

Supplementary Material Available: Kinetic measurements (Tables S1 and S2) (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the American Chemical Society; ordering information is given on any current masthead page.

OM9307287

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(56) The quality of the IR spectra was much better after dilution with acetonitrile.