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Article

Transition Metal Carbene Chemistry. 4. Nucleophilic Attachment of DABCO to Fischer Carbene Complexes in MeCN[†]

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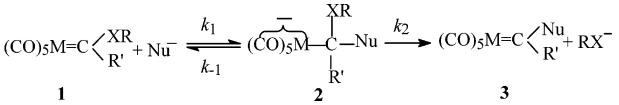
Rate constants for the attachment of DABCO (1,4-diazabicyclo[2.2.2]octane) to Fischer carbene complexes of the type $(CO)_5Cr{=}C(XR)C_6H_4Z$ ($X = O$ and S) in dry MeCN at 25 °C are reported. Hammett ρ values are 2.18 ± 0.13 and 0.89 ± 0.07 for DABCO reactions with $(CO)_5Cr{=}C(OMe)C_6H_4Z$ **(10-Cr-Z)** and $(CO)_5Cr{=}C(SMe)C_6H_4Z$ **(11-Cr-Z)**, respectively. The ρ values for the reaction of **10-Cr-Z** and **11-Cr-Z** with $CH(CN)_2^-$ in 50% MeCN–50% H_2O (v/v) are comparable to the present reactions. The reaction of DABCO with **10-Cr-Z** is more closely related to the reaction of $(n\text{-}Bu)_3P$ with $(CO)_5W{=}C(OMe)C_6H_5\text{-}Z$ (**23**) which also provided a ρ value 2.22. The much higher ρ values and hence much higher reactivity of methoxy carbene complexes over the corresponding thiomethyl derivatives fit a pattern observed previously for alkoxide ion, OH^-, amine, and thiolate ion nucleophiles, and a rational explanation comes from the consideration of the substituent effects not only on the transition state but also on the reactant. A major difference between **10-Cr-Z** and **11-Cr-Z** is that the π-donor effect of the methoxy group is much stronger than that of thiomethyl group. This leads to a substantial contribution of the zwitterionic form to the structure of **10-Cr-Z** with much more localized positive charge on the methoxy group than the negative charge on the $(CO)_5Cr$ moiety. This leads to overall destabilization by an electron-withdrawing phenyl substituents resulting an increase in reactivity. The ethoxycarbene complexes are somewhat less reactive than their methoxy counterparts due to the somewhat more ground state stabilization through its stronger π donor effect and partly due to steric crowding exerted by the slightly larger ethoxy group in the transition state. Higher $k_1(W)/k_1(Cr)$ ratios for (thiomethyl)carbene complexes than methoxy or ethoxycarbene complexes are related to the intrinsic rate constant which is higher for ((thiomethyl)carbene)tungsten complexes than the corresponding Cr ones resulting in an enhanced ratio.

Introduction

The extensive and ever increasing activity in the area of transition metal carbene complexes of the Fischer type has mainly been driven by their usefulness in organic synthesis. The key to the rich chemistry of this class of compounds is that they can undergo reactions at several sites: (i) modification of the carbene fragment; (ii) reactions on the sidearm; (iii) reactions on metal involving ligand exchange or change in oxidation state; (iv) insertion of unsaturated organic molecules into the metal−carbene bonds.[1] Of these, the most extensive studies have been made on the type i reactions, because most transition metal carbene complexes of the Fischer type are highly electrophilic at the carbene carbon.[1−3] Nucleophilic substitution of an alkoxy or akylthio group of carbene complexes such as **1** is one of the prototypical reactions of Fischer carbene complexes. It has generally been assumed to proceed via a tetrahedral intermediate **2** in analogy to the reaction of carboxylic esters with nucleophiles.



$$\mathrm{(CO)_5M{=}C}\langle^{\mathrm{XR}}_{\mathrm{R'}} + \mathrm{Nu^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overbrace{\mathrm{(CO)_5M}}^{-}{-}\underset{\mathrm{R'}}{\overset{\mathrm{XR}}{\mathrm{C}}}{-}\mathrm{Nu} \xrightarrow{k_2} \mathrm{(CO)_5M{=}C}\langle^{\mathrm{Nu}}_{\mathrm{R'}} + \mathrm{RX^-} \quad (1)$$

1 **2** **3**

Equation 1 shows the reaction scheme involving an anionic nucleophile, while reactions with neutral nucleophiles such as amines include a proton transfer as an additional step (eq 2).

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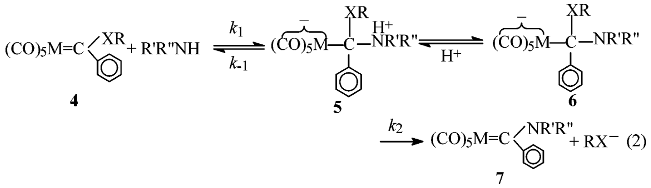
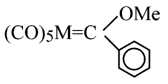


(2)

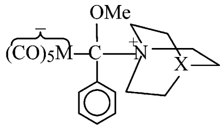
Most synthetic applications have involved common nucleophiles such as amines,[1,3,4−7] hydrazine,[1,8] oximes,[1,9] alkoxide ions,[1,3,10] thiolate ions,[1,3,11−13] and carbanions[13,14−18] (mainly aryl- and alkyllithium) as well as others.[1,19−21]

The first kinetic investigation of nucleophilic substitution reaction was that of Werner et al., who studied the reaction of **4** with several primary aliphatic amines (n-BuNH$_2$, C_6H_{11}-NH_2, $C_6H_5CH_2NH_2$) in n-decane, dioxane, methanol, and a dioxane−methanol (1:1) mixture showing complicated dependence on amine concentrations. There have been few other kinetic studies in the early literature; these investigations focused mainly on reactions with amines[3,22−24] and phosphines[3,25,26] in weakly polar organic solvents. More recently, a number of kinetic studies with alcohol,[27,28] alkoxide ions,[27,28] water,[29−33] OH$^-$,[29−33] thiol,[34−36] thiolate ions,[34−36] amines,[33,37−41] and carbanion[42] in polar (mainly water−acetonitrile mixtures) solvents were reported.

Though the postulate of tetrahedral intermediates generated by nucleophilic attack on the carbene carbon is reasonable, the studies discussed above provide no direct evidence for them. A direct support for such intermediates comes at least from the reaction of **8-Cr** and **8-W** with DABCO (X = N) or quinuclidine (X = CH) giving isolable tetrahedral adduct **9-Cr** and **9-W**.[27,43,44]

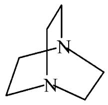


8-Cr (M= Cr), 8-W (M=W)

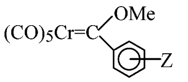


9-Cr & 9-W

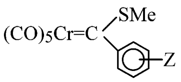
Generally tertiary amines possess drastically reduced nucleophilic character as a direct result of steric hindrance around the nitrogen (i.e. the bulky R groups) combined with the inability to generate neutral species (i.e. unable to lose a proton). Consequently, tertiary amines tend to react as bases rather than nucleophiles. Though DABCO is used as catalysts in many Baylis−Hillman type reactions,[45] to the best of our knowledge, there is no report on the kinetic studies on nucleophilic reactions of DABCO, particularly, with Fischer carbene complexes. We now report a kinetic investigation of the reaction of DABCO with **10-Cr-Z** (Z = Me$_2$N, MeO, Me, H, F, Cl, and CF$_3$), **11-Cr-Z** (Z = Me$_2$N, MeO, H, and F), and **12−14** in dry MeCN.



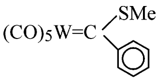
DABCO



10-Cr–Z



11-Cr–Z



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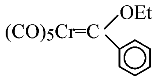

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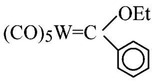

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Results

With neutral nucleophiles such as phosphines and amines, the nucleophilic attack on the carbene carbon leads to

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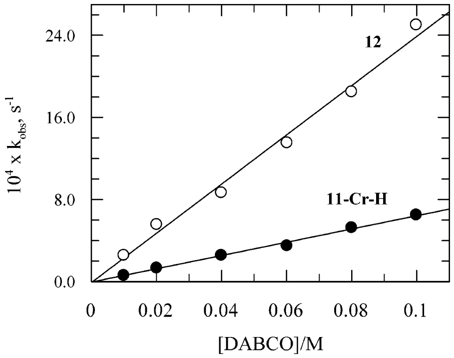
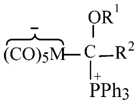


Figure 1. Representative Plots of k_{obs} (s^{-1}) vs [DABCO] for the reaction of DABCO with **11-Cr-H** and **12**.

Zwitterionic intermediates such **15**−**17**. If there is an acidic proton on the intermediate as in the case of **17**, the reaction can proceed further to product by elimination of ROH; otherwise the reaction stops at the adduct stage.



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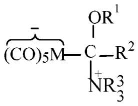

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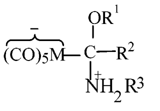
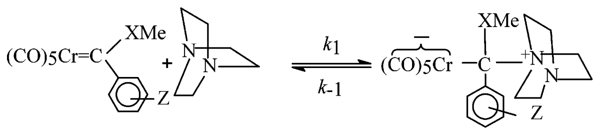


17

The reactions of DABCO with **10-Cr-Z** and **11-Cr-Z** lead to the respective adducts **18-Cr-Z** and **19-Cr-Z**, respectively, as shown in eq 3. As reported earlier, the time-resolved spectra leads to the loss of M = C chromophore resulting in a blue shift.[27]



(3)

10-Cr-Z (X=O)
11-Cr-Z (X=S)

18-Cr-Z (X=O)
19-Cr-Z (X=S)

The presence of isosbestic points indicates that the reaction is quite clean (spectra not shown). Formation of the addition product was confirmed for the case of **9-W** by isolating the synthesized product and comparing its UV/vis spectra with an infinity solution of a kinetic run.

Kinetic experiments were carried out in dry MeCN. Throughout the study pseudo-first-order conditions were maintained, with the carbene complexes as the minor component. All measurements were performed in a Hewlett-Packard 8453 Agilent diode array UV−vis spectrophotometer; rates were monitored at λ_{max} of the substrate.

For the reactions of DABCO with all the carbene complexes only one kinetic process was observed. Plots of k_{obsd}, the pseudo-first-order rate constant, versus [DABCO] were all linear with intercepts that were indistinguishable from zero (Figure 1). Second-order rate constants, interpreted as k_1 for nucleophilic attack and calculated as the slopes of plots of k_{obsd} versus [DABCO], are summarized in Table 1.

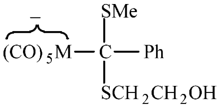
Discussion

Mechanism. The kinetic studies of the reactions of carbene complexes such as **10-Cr-Z** or **11-Cr-Z** along with **12**−**14** with a variety of nucleophiles have been reported in recent years.[3,22−41] $HOCH_2CH_2S^-$ was found to react with **11-Cr-H** or its tungsten analogue **12** reversibly to form the respective tetrahedral adducts **20**,[36] which were found to be quite stable particularly in the time scale of these experiments. The adducts do not proceed to the substitution product by expulsion of the MeS^- group, but upon addition of acid, they revert back to starting materials. These experiments allowed a determination of $k_1 = 6.60 \times 10^2$ M^{-1} s^{-1} as well as of $k_{-1} = 1.78 \times 10^{-3}$ s^{-1} and $K_1 = k_1/k_{-1} = 3.07 \times 10^5$ M^{-1}.[36]

Table 1. Rate Constants for the Reactions of DABCO with **10-Cr-Z**, **11-Cr-Z**, and $(CO)_5Cr{=}C(OEt)(Ph)$, $(CO)_5W{=}C(OMe)(Ph)$, $(CO)_5W{=}C(OEt)(Ph)$, and $(CO)_5W{=}C(SMe)(Ph)$ in Dry MeCN with $I = 0.10$ M ($NaClO_4$) and at 25 °C

Z	σ	10^2k_1	
		10-Cr-Z	11-Cr-Z
4-CF_3	0.54	172 ± 0.90	1.87 ± 0.08
3-Cl	0.37		0.37 ± 0.02
4-Cl	0.23		1.31 ± 0.03
4-F	0.06	23.4 ± 0.50	1.00 ± 0.02
4-H	0.00	18.4 ± 0.24	0.65 ± 0.02
4-Me	−0.17		0.42 ± 0.01
4-OMe	−0.27	5.14 ± 0.23	0.37 ± 0.02
4-NMe_2	−0.83	0.18 ± 0.01	0.13 ± 0.01

compd	k_1
$(CO)_5Cr{=}C(OEt)(Ph)$ (**13**)	$(6.45 \pm 0.51) \times 10^{-2}$
$(CO)_5W{=}C(OMe)(Ph)$ (**8-W**)	$(12.1 \pm 2.3) \times 10^{-2}$
$(CO)_5W{=}C(OEt)(Ph)$ (**14**)	$(10.5 \pm 0.25) \times 10^{-2}$
$(CO)_5W{=}C(SMe)(Ph)$ (**12**)	$(2.40 \pm 0.12) \times 10^{-2}$



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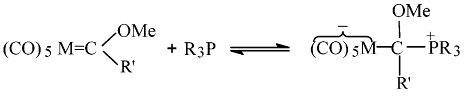
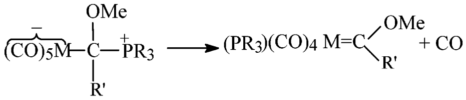
For the reactions of DABCO with **10-Cr-Z**, **11-Cr-Z**, and **12**−**14** the respective tetrahedral intermediates appears to be the final and stable (at least on the time scale of kinetics) products in dry MeCN. Hence only k_1, the rate constant for nucleophilic attack, could be determined for these reactions. The existence of no or negligible intercept precludes the determination of k_{-1} and hence K_1. With respect to the nucleophilic attack on the carbene carbon there are strong similarities between the reaction of phosphines or phosphites and that with DABCO. The reaction of phosphines are exemplified by eq 4.



(4)

21 **15**

However, **15** tends to rearrange to **22** by eq 5, a process



(5)

15 **22**

that is not observed with amine and other nucleophiles. Equilibrium constants determined by NMR techniques for

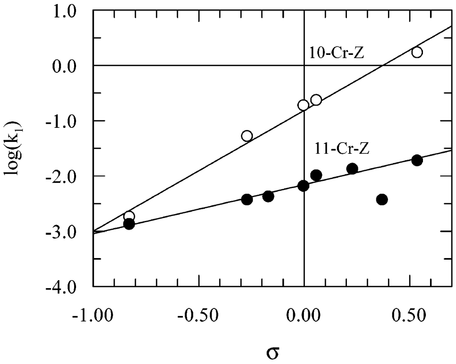
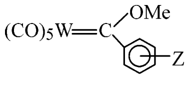


Figure 2. Hammett plots for the reaction of DABCO with **10-Cr-Z** and **11-Cr-Z** in dry MeCN.

the addition of several phosphines $(n\text{-Bu})_3P$, $(Ph\text{-}CH_2)_3P$, $(^iPr)_3P$ to $(CO)_5Cr{=}C(OMe)CH_3$ and to $(CO)_5W{=}C(OMe)CH_3$ in toluene-d_8 were reported by Fischer et al.[46-49] In the follow up study, Fischer investigated the temperature and substitutent effects on the equilibrium constant for the reaction of **23** ($Z = MeO$, Me, H, Br, and CF_3) in toluene with $(n\text{-Bu})_3P$.[50] A Hammett plot for log K_1 vs σ yielded $\rho = 2.22$; the point corresponding to Z = OMe deviates negatively by 0.90 log unit from the line.[50]



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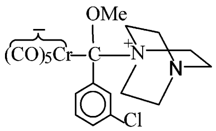
Kinetic studies for the reaction of PR_3 with $(CO)_5M = C(OMe)R'$ (M = Cr, Mo, and W, R = n-Bu and n-OBu, and R′ = Me and Ph groups) in acetone at 25 °C lead to the determination of rate constants both for the forward (k_1) and reverse (k_{-1}) reactions and hence equilibrium constants(K_1).[25] It was demonstrated that the sterric effect affects the k_{-1} values, while k_1 remains mostly unaffected, thereby leading to the change in K_1 values.

Hammett plots for the reactions of **10-Cr-Z** and **11-Cr-Z** with DABCO provide excellent linear fit with ρ values 2.18 ± 0.13 and 0.89 ± 0.07, respectively (Figure 2). The point corresponding to the reaction of **11-Cr-Cl**, where chlorine atom is at the *meta* position of the phenyl ring, deviates negatively by ~0.63 log unit. This departure mainly arises due to severe steric crowding at the carbene carbon in **24**.



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With respect to structure−reactivity relationships the following points are noteworthy.

(1) MeO vs MeS is an important consideration. With respect to rate constants (k_1) for the nucleophilic attachment of DABCO, it is the methoxycarbene complexes that are more reactive than thiomethyl analogues, indicating a higher intrinsic rate constants k_o(O) for the former than for the latter, k_o(S).[51] The higher intrinsic rate constants for the methoxy complexes can be understood in terms of the principle of nonperfect synchronization (PNS)[52] effects that result from transition state imbalances. Transition state imbalance arises mainly due to the following. (i) Steric effect: S being a larger atom, an early development of the steric effect reduces k_o(S) for thiomethyl carbene complexes more than k_o(O), for methoxycarbene complexes. (ii) Inductive effect: a disproportionately strong transition state stabilization by the inductive effect of O in methoxycarbene complexes over the S in the corresponding thiomethyl derivatives results in a lag in charge delocalization into the $(CO)_5M$ moiety and increases k_o(O) more than k_o(S). Though k_{-1} and K_1 and hence intrinsic rate constants cannot be determined to support our proposition, it is based mainly on the detailed analysis of the reactions of **8-Cr**,[35] **8-W**,[35] **11-Cr−H**,[36] and **12**[36] with $HOCH_2CH_2S^-$ and other thiolate ions. It has been revealed that the larger rate constants for **8-Cr** and **8-W** compared to that of **11-Cr-H** and **12** contrast with *lower equilibrium* constants for methoxy derivatives compared with thiomethyl derivatives. This means that the intrinsic barrier for the reaction of the thiomethyl derivative is higher, which was shown to result mainly from the large steric effect due to the bulky size of sulfur compared to that of oxygen that develops ahead of bond formation at the transition state.[36]

(2) As is the case for the reactions with OH^-,[32,42] n-$BuNH_2$,[38,40] piperidine,[39]$CH(CN)_2^-$,[42] and $HOCH_2CH_2S^-$,[34,36] nucleophilic attachment of DABCO to **8-Cr** is considerably faster than attachment to the corresponding thiomethyl derivative; the k_1(OMe)/k_1(SMe) ratio for DABCO (28.4) is virtually identical with the k_1(OMe)/k_1(SMe) ratio for $CH(CN)_2^-$ ($k_1(OMe) = 4.79 \times 10^3\ M^{-1}\ s^{-1}$; $k_1(SMe) = 1.46 \times 10^2\ M^{-1}\ s^{-1}$) (32.8) and for $HOCH_2CH_2S^-$ ($k_1(OMe) = 2.25 \times 10^4\ M^{-1}\ s^{-1}$; $k_1(SMe) = 6.60 \times 10^2$) (34.1) but smaller than for OH^- ($k_1(OMe) = 26.6\ M^{-1}\ s^{-1}$; $k_1(SMe) = 0.127\ M^{-1}\ s^{-1}$) (209) and n-$BuNH_2$ ($k_1(OMe) = 1.60 \times 10^3\ M^{-1}\ s^{-1}$; $k_1(SMe) = 9.56\ M^{-1}\ s^{-1}$) (167). In stark contrast, tertiary amines possess drastically reduced nucleophilic character as a direct result of steric hindrance around the nitrogen (i.e. the bulky R groups) combined with the inability to generate neutral species (i.e. unable to lose a proton). Consequently, tertiary amines tend to react as bases rather than nucleophiles. On the basis of the hard−soft acid−base concept [53,54] DABCO should behave as a moderately hard base and this ratio should correspond to the latter values, at least higher than the former values. The discrepancy in

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

(47) Kreissl, F. R.; Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 643.

(48) Kreissl, F. R.; Held, W. *J. Organomet. Chem.*, **1975**, *86*, C10.

(49) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Fischer, H. *Chem. Ber.* **1973**, *106*, 1262.

(50) Fischer, H. *J. Organomet. Chem.* **1979**, *170*, 309.

(51) The intrinsic rate constant is the rate constant in the absence of a thermodynamic driving force.

(52) The PNS states that if the development of a product-stabilizing factor lags behind changes or charge transfer at the transition state, k_0 is reduced. The same is true if the loss of a reactant-stabilizing factor runs ahead of bond change or charge transfer. For product-stabilizing factors that develop early or reactant-stabilizing factors that are lost late, k_0 is enhanced.

(53) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827.

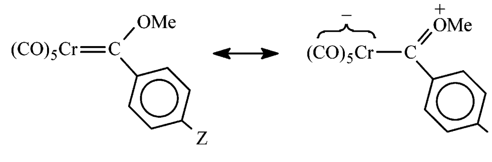
Table 2. Hammett ρ Values in 50% MeCN−50% Water (v/v) at 25 °C

nucleophiles	**10-Cr-Z**	**11-Cr-Z**
DABCO	2.18 ± 0.13^{a}	0.89 ± 0.07^{a}
$CH(CN)_2^-$	2.88 ± 0.26^{b}	0.69 ± 0.05^{b}
n-$BuNH_2$	2.20^{d}	0.59^{c}
MeO^- (MeOH)	2.03^{e}	
$HOCH_2CH_2S^-$		0.78^{f}
$(n\text{-}Bu)_3P$	2.20^{g}	
OH^-	2.20^{e}	1.16^{b}

[a] This work in pure MeCN. [b] Reference 42. [c] Reference 40. [d] Reference 39. [e] Reference 38. [f] $(CO)_5Cr{=}C(SCH_2CH_2OH)C_6H_5$-Z.[36] [g] $(CO)_5Cr{=}C(OMe)$-C_6H_5-Z.[36] [g] Reference 49.

reactivity pattern may be due to the relative importance of one over the other effects of the following factors: steric effects; hard−soft behavior; relative ground-state stability of the parent carbene complexes. Steric as well as hard−soft effects should increase the k_1(OMe)/k_1(SMe) ratio while ground-state stability of parent compounds disfavor the ncleophilic attack which is more for methoxycarbene complexes due to strong π-donor capacity of the oxygen over sulfur, which, hence, lowers the ratio. It is reasonable to think that the effect of ground-state stability predominates over the other factors leading to the decrease in k_1(OMe)/k_1(SMe) ratio.

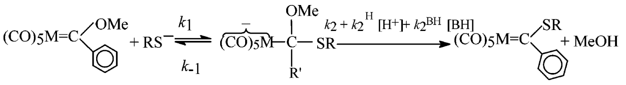
(3) Hammett plots for the reactions of DABCO with **10-Cr-Z** and **11-Cr-Z**, are shown in Figure 1. The ρ values are summarized in Table 2, along with ρ values for systems investigated previously. The ρ value for the reactions of DABCO with **10-Cr-Z,** methoxycarbene complexes (2.18 ± 0.13), is significantly larger than with **11-Cr-Z**, the thiomethyl derivatives (0.89 ± 0.07). The positive ρ values imply that electron-withdrawing substituents stabilize the adduct **18** and/or destabilize the carbene complexes. Since in the adduct there are both positive and negative charges, the net substitutent effect on this species cannot be very large; in view of the fact that negative charge is more dispersed than the positive charge, an argument could be made that there should actually be a slight net destabilization of **18**. Hence, main factor that can account for the positive ρ values is a destabilization of the carbene complexes, which is best understood in terms of an increased electron deficiency on the carbene carbon. Thus, the key to an understanding of these findings is to consider the substituent effect not only on the transition state but also on the reactant. A major difference between **10-Cr-Z** ($\rho = 2.18$) and **11-Cr-Z** ($\rho = 0.89$) is that the π-donor effect of the methoxy group is much stronger than that of the thiomethyl group[55] and leads to a substantial contribution of the zwitterionic form **25** to the structure of **10-Cr-Z**. Since the positive charge on the methoxy group is much more localized than the negative charge on the $(CO)_5Cr$ moiety, the overall effect of an electron-withdrawing phenyl substituent will be destabilizing and hence result in an increased reactivity of the carbene complex.



(6)

10-Cr-Z **25**

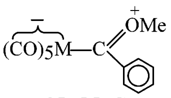
(4) Cr vs W is an important factor. The higher k_1 values for the reactions of DABCO with the tungsten carbene complexes compared to the corresponding chromium carbene complexes (k_1(**12**)/k_1(**11-Cr-H**) = 3.98; k_1(**8-W**)/k_1(**8-Cr**) = 1.80; k_1(**14**)/k_1(**13**) = 1.62) follows previously observed patterns.[27,30,35] Nucleophilic addition to the tungsten carbene complexes is slightly favored over the addition to chromium complexes. The effect on equilibrium constant (K_1) is small but somewhat larger on k_1 for the reaction of **11-Cr-H** and **12** with various thiolate ions (eq 7).



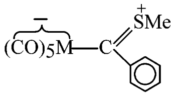
(7)

8-M **26** **27**

The K_1(W)/K_1(Cr) ratios vary between 1.27 and 1.53, while k_1(W)/k_1(Cr) ratios vary between 2.56 and 3.54. Similar results were obtained for the MeO^- addition with K_1(W)/K_1(Cr) = 1.58 and k_1(W)/k_1(Cr) = 2.41. The rather small dependence of K_1 on metal may be the result of the extensive dispersion of the negative charge into the CO ligands of the adducts. Since this leaves little charge on the metal, the identity of the metal has only a small influence on the stability of the adduct. An additional factor is related to the strong contribution of **25** to the structure of **10-Cr-Z** and **8-W**, because **25** leads to substantial negative charge on the $(CO)_5M$ moiety of the carbene complexes; the presumably greater stabilization of the negative charge by the $(CO)_5W$ moiety in the adduct is partially offset by a similar effect on the carbene complex. The higher (k_1(W)/k_1(Cr) ratio for thiomethylcarbene complexes compare to the methoxy- or ethoxycarbene complexes can also be judged from the above point of view.



25, M=Cr
28, M= W



29, M=Cr
30, M= W

The resonance structures **29** and **30** are of lesser importance than **25** and **28**, and hence, there is less negative charge on the $M(CO)_5$ moieties of **11-Cr-H** and **12** than those of **8-Cr** and **8-W**. As a result there is less compensation and higher value of (k_1(W)/k_1(Cr) ratio.

(5) Finally, we consider MeO vs EtO. The ethoxycarbene complexes are somewhat less reactive than their methoxy counterparts. This arises due to the somewhat stronger π-donor effect of the ethoxy group and hence more ground-state stabilization over to that of the methoxy group and partly due to steric crowding exerted by the slightly larger

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(54) (a) Pearson, R. G. *Surv. Prog. Chem.* **1969**, *5*, 1. (b) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734. (c) Hati S.; Datta, D. *Proc. Indian Acad. Sci., Chem. Sci.* **1996**, *108*, 143.
(55) ρ(OMe) = −0.42;[56] ρ(SMe) = −0.15.[56]
(56) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

ethoxy group in the transition state, which corresponds to a pattern observed earlier.[30,35]

Experimental Section

Materials. DABCO (Aldrich) was analytical grade and was purified by the sublimation method. Acetonitrile (Fischer Scientific) was used as received. MeCN was distilled over CaH_2 before use. The carbene complexes used as substrates were synthesized and characterized as described in the previous studies[28,30,42]

Synthesis of 9-W. The ylide products of the reaction of **8-W** with DABCO was synthesized as follows: A 0.222 g (0.5 mmol) amount of **8-W** was dissolved in 20 mL of dry acetonitrile in a round-bottom flask under Ar atmosphere. To this solution was added 2 mmol of DABCO in 15 mL of acetonitrile. The mixture was allowed to react for 1 h whereupon the solvent was removed under high vacuum. The solid product was dissolved in a minimum volume of 50% MeCN−50% CH_2Cl_2 (v/v) and charged on a silica gel column prepared with the same solvent mixture. The yellow band was collected and dried under high vacuum to get the crystalline solid. ^1H NMR [δ ($CDCl_3$)]: 3.31 (s, 3H, CH_3O), 3.34 (m, 6, NCH_2), 3.65 (m, 6, $^+NCH_2$), 7.47 (m, 5, C_6H_5).

Instrumentation and Kinetic Experiments. NMR spectra were recorded on a Bruker 300 MHz instrument. UV−vis spectra were obtained on an Agilent 8453 diode array spectrophotometer.

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