ORGANOMETALLICS

Effect of pressure on the insertion kinetics of metal-carbene complexes

K. J. Schneider, A. Neubrand, R. Van Eldik, and H. Fischer

Organometallics, **1992**, 11 (1), 267-269• DOI: 10.1021/om00037a048 • Publication Date (Web): 01 May 2002

Organometallics **1992,** *11,* 267–269 267

Effect of Pressure on the Insertion Kinetics of Metal–Carbene Complexes

K. J. Schneider, A. Neubrand, R. van Eldik,* and H. Fischer[1]

Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, FRG

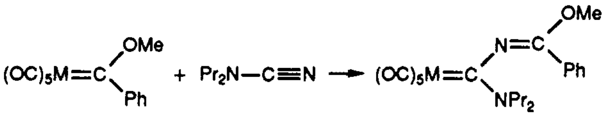
Received July 8, 1991

Kinetic studies on the insertion of electron-rich triple-bonding systems such as dipropylcyanamide and 1-(diethylamino)propyne into the metal–carbene bond of pentacarbonyl(methoxyphenylcarbene)chromium and -tungsten as a function of pressure were performed using UV–vis techniques. All investigated reactions exhibit a marked pressure acceleration. The substantially negative volumes of activation (–17 to –25 cm^3 mol^{-1}) and the strongly negative entropies of activation (–128 to –146 J K^{-1} mol^{-1}) are in accordance with earlier studies that proposed a three-step mechanism with considerable bond formation in the rate-determining step. Furthermore, by comparison of the volumes of activation, the influence of the size of the metal center on the structure of the transition state can be discussed.

Introduction

High-pressure kinetic techniques have recently been successfully used to assist in the elucidation of the intimate reaction mechanisms of ligand substitution processes of metal carbonyl complexes in solution.[2-8] The reported volumes of activation, estimated from the pressure dependence of the observed rate constants, exhibit a marked sensitivity for the nature of the metal center and the bulkiness of the entering and leaving groups. These studies indicated that we are dealing with a sensitive mechanistic parameter for thermal as well as photochemical[9-11] substitution processes in organometallic chemistry.

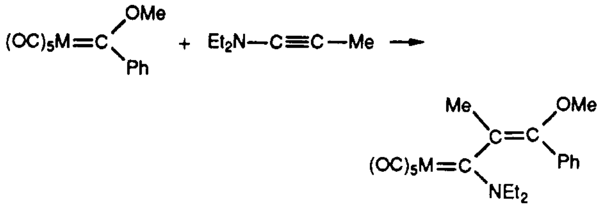
In the mentioned processes the reaction occurs on the metal center and involves a partial change in the coordination number during the activation process. In this respect we became interested in the effect of pressure on insertion reactions of metal carbene complexes in which nucleophilic attack occurs at the carbene carbon center. Such complexes play an essential role in the catalysis of olefin metathesis and polymerization reactions. For this purpose insertion of dipropylcyanamide and 1-(diethylamino)-1-propyne into the metal–carbene bond of (methoxyphenylcarbene)pentacarbonylchromium and -tungsten was selected for this investigation. The overall insertion reactions are presented in (1) and (2) respectively, where M = Cr and W.



$$(OC)_5M{=}C(OMe)Ph + Pr_2N{-}C{\equiv}N \longrightarrow (OC)_5M{=}C(NPr_2){-}N{=}C(OMe)Ph \quad (1)$$

Experimental Section

Materials. The (methoxyphenylcarbene)pentacarbonyl complexes and 1-(diethylamino)-1-propyne were synthesized at the University of Konstanz according to the details published before.[12,13] Di-*n*-propylcyanamide was synthesized from bromocyanide (Merck) and di-*n*-propylamine (Merck) and purified by fractional distillation.[14] The solvents methylcyclohexane (Fluka) and octane (Janssen) were dried and fractionally distilled from potassium–sodium alloy before use and stored under argon. Test solutions were transferred to optical cuvettes, pillbox cells,[15] and syringes for UV–vis spectroscopic and kinetic measurements under anaerobic conditions.



$$(OC)_5M{=}C(OMe)Ph + Et_2N{-}C{\equiv}C{-}Me \longrightarrow (OC)_5M{=}C(NEt_2){-}C(Me){=}C(OMe)Ph \quad (2)$$

Instrumentation. UV–vis spectra were recorded on Shimadzu UV 250 and Hitachi U-3200 spectrophotometers. Slow kinetic measurements were performed in the thermostated (±0.1 °C) cell compartments of these spectrophotometers at ambient pressure, and in a thermostated high-pressure cell[16] built into a Zeiss PMQ II spectrophotometer for pressures up to 150 MPa. Fast reactions were studied on a modified Aminco stopped-flow instrument at ambient pressure and on a homemade high-pressure stopped-flow unit[17] for pressures up to 100 MPa. Both instruments were thermostated (±0.1 °C) with an external cryostat, and data acquisition and handling were performed on an on-line computer system.[18] The insertion reactions were studied under pseudo-first-order conditions, i.e. a large excess of nucleophile, and the corresponding first-order plots were linear for at least 2–3 half-lives of the reaction.

Results and Discussion

Both reactions 1 and 2 are characterized by significant spectral changes at ca. 400 nm that are associated with the disappearance of the pentacarbonyl(methoxyphenylcarbene) charge-transfer band. The observed pseudo-first-order rate constants exhibit a linear dependence on the nucleophile concentration, as can be seen from the rate data summarized for these reactions in Tables I and II, respectively. The plot of k_{obs} versus the cyanamide concentration exhibits a small intercept that can be neglected

---

[1] Fakultät für Chemie, Universität Konstanz, Universitätsstrasse 10, 7750 Konstanz 1, FRG.

[2] van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989,** *89,* 549.

[3] Awad, H. H.; Dobson, C. B.; Dobson, G. R.; Leipoldt, J. G.; Schneider, K. J.; van Eldik, R.; Wood, H. E. *Inorg. Chem.* **1989,** *28,* 1654.

[4] Schneider, K. J.; van Eldik, R. *Organometallics* **1990,** *9,* 1235.

[5] Bal Reddy, K.; van Eldik, R. *Organometallics* **1990,** *9,* 1418.

[6] Zhang, S.; Dobson, G. R.; Bajaj, H. C.; Zang, V.; van Eldik, R. *Inorg. Chem.* **1990,** *29,* 3477.

[7] Zhang, S.; Zang, V.; Bajaj, H. C.; Dobson, G. R.; van Eldik, R. *J. Organomet. Chem.* **1990,** *397,* 279.

[8] Wieland, S.; van Eldik, R. *Organometallics* **1991,** *10,* 3110.

[9] Wieland, S.; van Eldik, R. *Coord. Chem. Rev.* **1990,** *97,* 155.

[10] Wieland, S.; Bal Reddy, K.; van Eldik, R. *Organometallics* **1990,** *9,* 1802.

[11] Wieland, S.; van Eldik, R. *J. Phys. Chem.* **1990,** *94,* 5865.

[12] Fischer, H.; Dötz, K. H. *Chem. Ber.* **1980,** *113,* 193.

[13] Fischer, H.; Märkl, R. *Chem. Ber.* **1985,** *118,* 3683.

[14] Wallach, O. *Ber. Deutsch. Chem. Ges.* **1899,** *32,* 1872.

[15] le Noble, W. J.; Schlott, R. *Rev. Sci. Instrum.* **1976,** *47,* 770.

[16] van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* **1981,** *50,* 131.

[17] Kraft, J.; Wieland, S.; Kraft, U.; van Eldik, R. *GIT Fachz. Lab.* **1987,** *31,* 560.

[18] Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963,** *85,* 866.

0276-7333/92/2311-0267$03.00/0

Table I. k_{obs} as a Function of Concentration, Temperature, and Pressure for Reaction 1[a]

M	$[Pr_2N-C\equiv N]$, M	temp, °C	pressure, MPa	10^4k_{obs},[b] s^{-1}
Cr	0.0272	28.2	2	0.525 ± 0.004
	0.0734			1.47 ± 0.03
	0.116			2.09 ± 0.03
	0.154			2.45 ± 0.10
	0.202			4.05 ± 0.19
	0.154	19.3	2	1.5 ± 0.1
		28.2		2.5 ± 0.1
		37.7		4.9 ± 0.2
		42.3		6.6 ± 0.2
		50.2		12.6 ± 0.4
	0.154	28.2	5	2.5 ± 0.1
			50	3.3 ± 0.1
			100	4.8 ± 0.2
			150	6.8 ± 0.2
W	0.010	61.4	2	0.198 ± 0.001
	0.040			0.33 ± 0.01
	0.155			1.30 ± 0.01
	0.212			1.43 ± 0.03
	0.297			2.70 ± 0.12
	0.317			3.3 ± 0.2
	0.152	48.2		0.744 ± 0.006
		66.5		1.79 ± 0.06
		74.1		3.38 ± 0.25
		79.5		4.68 ± 0.06
	0.151	60.4	5	1.37 ± 0.05
			50	1.99 ± 0.06
			100	2.98 ± 0.20
			150	4.00 ± 0.02

[a] [M] = 1 × 10^{-4} M; solvent = methylcyclohexane. [b] Mean value of at least three kinetic runs.

Table II. k_{obs} as a Function of Concentration, Temperature, and Pressure for Reaction 2[a]

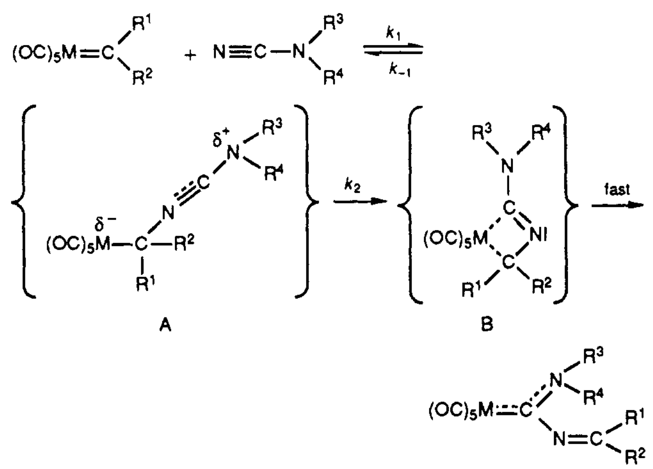
M	$[Et_2NC\equiv CMe]$, M	temp, °C	pressure, MPa	10^2k_{obs},[b] s^{-1}
Cr	0.110	30.2	6	3.25 ± 0.02
			25	3.84 ± 0.07
			50	4.31 ± 0.19
			74	5.54 ± 0.15
			100	6.99 ± 0.15
W	0.0155	25.0	0.1	1.53 ± 0.03
	0.0327			3.40 ± 0.05
	0.0663			6.70 ± 0.10
	0.0219	16.5		1.35 ± 0.05
		22.2		1.79 ± 0.03
		28.9		2.41 ± 0.05
	0.0323	25.0	5	3.25 ± 0.09
			25	4.22 ± 0.04
			50	5.42 ± 0.07
			75	6.64 ± 0.07
			100	8.6 ± 0.3

[a] [M] = 1 × 10^{-4} M; solvent = octane. [b] Mean value of at least three kinetic runs.

at higher nucleophile concentrations. The reported data are in agreement with earlier observations.[12,13] Kinetic data for the temperature and pressure dependence of reactions 1 and 2 were recorded at a fixed nucleophile concentration, and the results are also included in Tables I and II, respectively. The activation parameters $\Delta H^‡$ and $\Delta S^‡$ were calculated from an Eyring plot using a least-squares fitting routine. Plots of ln k_{obs} versus pressure are linear for all the data sets, and $\Delta V^‡$ was calculated from the slope of these plots $(=-\Delta V^‡/RT)^2$ in the usual way. All the rate and activation parameters for the investigated reactions are summarized in Table III.

It can be seen from the data in Table III that the investigated reactions all exhibit rather similar rate and activation parameters. The observed first-order dependence on the nucleophile concentration, the relatively low $\Delta H^‡$ values (31–52 kJ mol^{-1}), the strongly negative $\Delta S^‡$ values (−128 to −146 J K^{-1} mol^{-1}), and the significant negative $\Delta V^‡$ values (−17 to −25 cm^3 mol^{-1}) are all in agreement with an associative bond formation process in which we are dealing with a highly structured transition state. Furthermore, a number of observations support the nucleophilic nature of the bond formation process:[12,13,18] An increase in the donor strength of the alkyl group in R_2N–CN increases the observed second-order rate constant; the log k values correlate with the sum of the Taft constants; the introduction of an electron acceptor substituent in the para position of the phenyl group also increases the observed second-order rate constant.[19] In addition, detailed theoretical calculations indicate that the nucleophilic attack occurs on the carbene carbon and not on the carbonyl carbon atoms.[18,20] This is further supported by a good correlation found between the rate constant of reaction 2 and the equilibrium constant for the reversible addition of PBu_3 to the employed carbene.[21,22] From the product distribution and the steric effect of the substituents on R_2N–CN on the observed rate constants, it can be concluded that the cyanamide attacks the carbene atom mainly via the nitrile nitrogen atom.[13] This is accompanied by some charge separation between the metal center and the adjacent carbon atom.[20]

Scheme I



The above outlined arguments can be summarized by the mechanism given in Scheme I.[13] Theoretical calculations indicate that the cyclic state B is at an energy maximum and therefore does not represent an intermediate species, but rather a transition state.[20] Under pseudo-first-order conditions the rate law for this mechanism is given in (3), which has two limiting forms de-

$$k_{obs} = k_1k_2[Nu]/(k_{-1} + k_2) \quad (3)$$

pending on the magnitude of k_{-1} and k_2. It has been argued that the very negative $\Delta S^‡$ value (expressed in terms of the preexponential Arrhenius factor) supports the assumption that $k_{-1} \gg k_2$,[13] such that (3) reduces to (4). It

$$k_{obs} = k_1k_2[Nu]/k_{-1} = K_1k_2[Nu] \quad (4)$$

follows that attack of the nucleophile at the carbene carbon can be considered as a rapid preequilibrium, followed by the formation of the metallacycle as the rate-determining step. In terms of this model, B can be considered to rep-

---

(19) Fischer, H. *J. Organomet. Chem.* **1980**, *197*, 303.

(20) Märkl, R. Doctoral Dissertation, Technische Universität München, FRG, 1983.

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

(22) Fischer, H. *J. Organomet. Chem.* **1979**, *170*, 181.

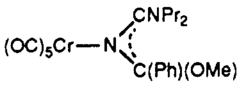
Table III. Rate and Activation Parameters for the Insertion Reactions[a] (1) and (2)

complex	ligand	k, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J $K^{-1}\ mol^{-1}$	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$
$(OC)_5CrC(Ph)(OMe)$	$Pr_2N—CN$	$(1.9 \pm 0.2) \times 10^{-3}$ (at 28.1 °C)	51 ± 3	−128 ± 10	−17.3 ± 0.3
$(OC)_5WC(Ph)(OMe)$		$(9 \pm 1) \times 10^{-4}$ (at 61.4 °C)	52.1 ± 0.6	−146 ± 2	−20.7 ± 1.1
$(OC)_5CrC(Ph)(OMe)$	$Et_2N—C{\equiv}CMe$	0.26[b] (at 20 °C)	33 ± 4[b]	−142 ± 12[b]	−20.2 ± 1.4
$(OC)_5WC(Ph)(OMe)$		1.01 ± 0.03 (at 25 °C)	31.5 ± 0.7	−140 ± 2	−24.7 ± 1.0
		0.87[b] (at 20 °C)	32.7 ± 1.7[b]	−134 ± 6[b]	

[a] Experimental data reported in Tables I and II. Quoted activation parameters are for the second-order rate constant k_1k_2/k_{-1} (=k_{obs}/[Nu]). [b] Data reported in ref 12.

resent the transition-state structure. This would further account for the minor solvent dependence observed for such insertion reactions.[13]

In terms of the $\Delta V^{\ddagger}$ data reported in this study, it follows from (4) that $\Delta V^{\ddagger} = \Delta \bar{V}(K_1) + \Delta V^{\ddagger}(k_2)$, i.e. the sum of the reaction volume for the formation of A and the activation volume for the rate-determining step k_2. It is reasonable to expect that both these quantities will be negative since they both involve bond formation processes. In general, addition as well as oxidative addition reactions are characterized by markedly negative volumes of activation.[2] The intrinsic volume collapse for the formation of A could in principle be only a few $cm^3\ mol^{-1}$ since state A does not represent a very effective overlap of the reactant spheres. However, state A does represent some partial charge separation that could cause some solvent electrostriction and a subsequent decrease in volume. Furthermore, on going from A to B, the cyclization process is expected to cause a significant decrease in volume. A similar mechanism can be assumed to be valid for the insertion of the aminopropyne,[12] such that it is quite reasonable that the overall $\Delta V^{\ddagger}$ is very similar for all investigated reactions. It therefore seems reasonable to conclude that $\Delta \bar{V}(K_1)$ and $\Delta V^{\ddagger}(k_2)$ contribute to the same extent, i.e. both ca. −10 $cm^3\ mol^{-1}$, to the overall $\Delta V^{\ddagger}$ value. The formation of a cyclic, quasi 7-coordinate state B for M = Cr does not seem to be in agreement with $\Delta V^{\ddagger}$ data reported for ligand substitution reactions of related chromium carbonyl complexes.[6,7,23,24] The latter data favor the operation of a dissociative or at most an interchange ligand substitution process on the relatively small chromium center. However, it should be kept in mind that state B is suggested to be a transition-state species, which in the case of M = Cr could have a more linear type T structure, similar to C, in which the nucleophile slips past the metal center to move to its final binding position. Such a slippage process would also cause a significant drop in volume and does not require the ultimate formation of a quasi 7-coordinate transition state for M = Cr, although such a state is not impossible.[25] In fact this minor difference in the geometry of the transition state of M = W and Cr, viz. cyclic compared to T structure, could account for the difference of ca. 4 $cm^3\ mol^{-1}$ in the $\Delta V^{\ddagger}$ values (Table III) for these complexes, since the cyclic transition state is expected to be more compact than the T type structure. Alternatively, the difference of ca. 4 $cm^3\ mol^{-1}$ for the W and Cr complexes could arise from the degree of M–C bond formation in B, which could be significantly less for Cr, due to the above-outlined reasons, than for W.



C

Finally, the observed pressure acceleration is in good agreement with that recently reported for auxiliary [2 + 2] cycloaddition reactions of Fischer type carbene complexes.[26] The latter reactions exhibit no significant solvent dependence, and the observed $\Delta V^{\ddagger}$ values of ca. −16 $cm^3\ mol^{-1}$ were interpreted in terms of intrinsic volume changes associated with a concerted, almost synchronous bond formation process. The more negative $\Delta V^{\ddagger}$ values reported in this study may result from the preassociation equilibrium suggested in Scheme I. All in all, both insertion and cycloaddition reactions of metal carbonyl complexes seem to undergo a significant pressure acceleration, an effect that can be employed to either assist mechanistic analyses or to improve synthetic possibilities.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagen-Stiftung.

Registry No. $(OC)_5CrC(Ph)(OMe)$, 27436-93-7; $(OC)_5WC(Ph)(OMe)$, 37823-96-4; $Pr_2N—CN$, 1531-36-8; $Et_2N—C{\equiv}CMe$, 4231-35-0.

---

(23) Bal Reddy, K.; van Eldik, R. *Organometallics* **1990**, *9*, 1418.

(24) Zhang, S.; Zang, V.; Dobson, G. R.; van Eldik, R. *Inorg. Chem.* **1991**, *30*, 355.

(25) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194.

(26) Pipoh, R.; van Eldik, R.; Wang, S. L. B.; Wulff, W. D. *Organometallics*, in press.