Journal of Organometallic Chemistry, 440 (1992) 113–117
Elsevier Sequoia S.A., Lausanne
JOM 22914

Effect of pressure on intramolecular ring-closure reactions of molybdenum carbonyl complexes induced by flash photolysis

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(Received April 8, 1992)

Abstract

A laser flash-photolysis study has been made of the pressure-dependence of a series of ring-closure reactions of the type $Mo(CO)_5L\text{–}L \rightarrow (CO)_4Mo(\overset{\frown}{L\ L}) + CO$ where L–L represents 1,10-phenanthroline (phen) and a series of substituted phen ligands. The results demonstrate that the ring-closure of such rigid chelates occurs by an interchange mechanism in which bond-forming and bond-breaking at the Mo centre occur to similar extents in the transition state independent of the nature of the phen chelate.

Introduction

There is a continued interest in details of the mechanism of ligand substitution reactions of metal carbonyl complexes, especially of those of the Group VIB metals owing to their important role in catalytic processes [1–3]. Many systems have been studied in great detail and the use of high pressure kinetic techniques has contributed to a clarification of the underlying mechanisms [4–10]. More recently, flash photolysis techniques have been used to study the behaviour of coordinatively unsaturated species and their solvent-coordinated analogues produced from the hexacarbonyl complexes as shown in eq. 1 [11]. In the presence of a

$$\begin{aligned} M(CO)_6 &\xrightarrow{h\nu} M(CO)_5 + CO \\ M(CO)_5 + \text{solv} &\longrightarrow M(CO)_5(\text{solv}) \end{aligned} \qquad (1)$$

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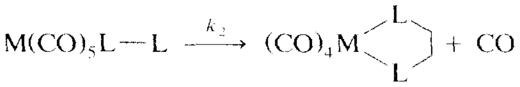
nucleophile L, the solvent complex undergoes reaction as shown in eq. 2. Such solvent complexes are very labile and usually short-lived species, and can therefore only be studied by fast kinetic techniques such as flash photolysis and, in the case

$$M(CO)_5(solv) + L \xrightarrow{k_1} M(CO)_5L + solv \qquad (2)$$

of more strongly coordinated solvents, stopped-flow methods. Because of the high reactivity of such complexes they may represent the main intermediates in homogeneously catalyzed reactions even when they are present at extremely low concentrations in solution. The application of high pressure flash-photolysis techniques to their study [12–14] has assisted the understanding of the detailed reaction mechanism. The results demonstrated that the nature of the metal center, in particular its size (M = Cr, Mo, W), the coordination mode and coordinating ability of the solvent, and the size and nucleophilicity of the entering ligand can all contribute to control the intimate mechanism of the solvent displacement reaction 2. The observed volumes of activation clearly demonstrated the balance between the importance of bond-forming and bond-breaking processes at the metal center, and a gradual changeover from more dissociative (*D* or I_d) to more associative (*A* or I_a) substitution processes was observed on increase in size of the metal center [13,15].

When the entering nucleophilic is a bidentate species L–L, reaction 2 is followed by a slower ring-closure reaction to give the more stable tetracarbonyl complex, as shown in eq. 3. This reaction involves the thermal displacement of a coordinated CO molecule and is again of fundamental importance to catalytic



$$M(CO)_5L{-}L \xrightarrow{k_2} (CO)_4M\left\langle\begin{matrix}L\\L\end{matrix}\right] + CO \qquad (3)$$

cycles involving the binding and release of such molecules on metal centers. In this case also the application of high pressure kinetic techniques has assisted the elucidation of the detailed reaction mechanism [16–18]. The available data suggest that the nature of the ring-closure mechanism is controlled by the size of the metal center (M = Cr, Mo, W) and the steric hindrance at the non-coordinated end of the chelate ligand L–L. We have recently demonstrated that increasing steric hindrance in the bipyridine ligand can cause a change-over in mechanism from I_a to I_d for ring-closure of the corresponding pentacarbonyl molybdenum complexes [19].

In the present study we have investigated the ring-closure reactions of a series of complexes of the type $Mo(CO)_5L{-}L$, where L–L denotes 1,10-phenanthroline (phen) or a substituted-phen. Phenanthroline is a significantly more rigid ligand than bipyridine and is expected to exhibit less flexibility during ring-closure reactions.

Experimental section

$Mo(CO)_6$ (Aldrich) was vacuum-sublimed before use. The phenanthroline ligands (Aldrich) were used without further purification. Toluene was distilled from Na under nitrogen. All solutions were prepared under a nitrogen atmosphere by Schlenk techniques. The $Mo(CO)_5L{-}L$ species were prepared in solution by flash photolysis of mixtures of $Mo(CO)_6$ and L–L in toluene in a three window high pressure cell [20] using a pillbox optical cell [21]. The studies were carried out by use of a Quanta-Ray DCR-2 Nd: YAG laser operating at 355 nm (100 mJ; 5–6 ns fwhi), an Oriel 75 W Xenon lamp, and a Durrum monochromator. The photolysis beam intersected the analysing beam at right angles in the high pressure cell. Samples were stirred between experiments with the aid of a small Teflon-coated stirring bar in the optical cell and an external magnetic stirrer. The kinetic traces were recorded on a LeCroy 9400 oscilloscope interfaced to an IBM compatible PC. The first order rate constants for the ring-closure reaction, k_2, were obtained as averages of 5–10 kinetic traces, and the volumes of activation were calculated from the slopes ($= -\Delta V^{\#}/RT$) of the plots of ln k_{obs} versus pressure. Such plots were linear within experimental error.

Results and discussion

The values of k_2 as a function of pressure for a series of ring-closure reactions along with the corresponding $\Delta V^{\#}$ values are summarized in Table 1. In most cases the reactions exhibit a slight decrease in k_2 with increase in pressure, indicating a small positive volume of activation. The presence of methyl substituents on the phen ligand tends to cause a slight increase in $\Delta V^{\#}$, which could mean that Mo–CO bond cleavage is more advanced in the transition state for the

Table 1

Kinetic data for the ring-closure of $Mo(CO)_5L$–L as a function of pressure in toluene at 25°C

L–L	Pressure (MPa)	$k_2 \times 10^{-3}$ (s^{-1})	$\Delta V^{\#}$ ($cm^3\ mol^{-1}$)
phen	0.1	3.61 ± 0.12	+ 0.6 ± 0.2
	50	3.51 ± 0.07	
	100	3.49 ± 0.12	
	150	3.48 ± 0.09	
2,9-Me_2phen	0.1	0.237 ± 0.023	− 0.1 ± 0.4
	25	0.235 ± 0.020	
	100	0.237 ± 0.016	
	150	0.230 ± 0.024	
4,7-Me_2phen	0.1	0.232 ± 0.030	+ 1.5 ± 0.3
	25	0.227 ± 0.035	
	50	0.228 ± 0.038	
	100	0.223 ± 0.040	
	150	0.210 ± 0.011	
5-Clphen	0.1	1.76 ± 0.18	+ 3.3 ± 0.5
	25	1.70 ± 0.21	
	50	1.65 ± 0.15	
	100	1.48 ± 0.10	
	150	1.46 ± 0.12	
3,4,7,8,-Me_4phen	0.1	3.30 ± 0.17	+ 2.3 ± 0.4
	25	3.20 ± 0.30	
	50	3.02 ± 0.34	
	100	2.98 ± 0.26	
	150	2.85 ± 0.14	

Table 2

Comparison of ring-closure rate constants and volumes of activation at 25°C for the reaction of $Mo(CO)_5L{-}L$ [a]

Solvent	L–L	k_2 (s^{-1})	$\Delta V^{\#}$ ($cm^3\ mol^{-1}$)	Ref.
Tol	en	3.0×10^{-5}	-5.4 ± 0.8	17
Tol	$dabR_2$	1.1×10^{-3}	-9.5 ± 0.4	17
Tol	bpy	3.1	-3.9 ± 0.6	19
Tol	4,4′-Me_2bpy	2.6	-5.6 ± 0.4	19
Tol	4,4′-Ph_2bpy	1.4	$+5.4 \pm 0.5$	19
FB	phen	1.1×10^{4}	-2.9 ± 0.2	18
Tol	phen	3.6×10^{3}	$+0.6 \pm 0.2$	[b]
tol	5-Clphen	1.8×10^{3}	-0.1 ± 0.4	[b]
Tol	4.7-Me_2phen	2.3×10^{2}	$+1.5 \pm 0.3$	[b]
Tol	2,9-Me_2phen	2.4×10^{2}	$+3.3 \pm 0.5$	[b]
Tol	3,4,7,8-Me_4phen	3.3×10^{3}	$+2.3 \pm 0.4$	[b]

[a] Abbreviations used: Tol = toluene, FB = fluorobenzene, en = ethylenediamine, $dabR_2$ = 1,4-diisopropyl-1,4-diazabutadiene, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline. [b] This work.

ring-closure of the bulkier phen ligands. However, the overall effect is small and the $\Delta V^{\#}$ data in Table 1 are, in general, in agreement with the concept of an interchange (I) mechanism [5]. In this case the volume collapse associated with Mo–N bond formation is balanced out by the volume increase associated with Mo–CO bond cleavage in the transition state of the ring-closure reaction.

The results of this study are compared with those for related ring-closure reactions in Table 2. Only one set of data is at present available for the ring-closure in another solvent, namely the ring-closure of $Mo(CO)_5$phen in fluorobenzene; in that case the reaction is significantly faster and shows a more negative value of $\Delta V^{\#}$ than does the reaction in toluene. This could mean that fluorobenzene favours an earlier transition state in which more bond-forming and less bond-breaking occur in the transition state, *i.e.* an I_a mechanism. Again, the effects are small and should be interpreted with caution. Comparison of the ring-closure data for the series of bpy and phen complexes does reveal some interesting features. The much slower bpy reactions exhibit a remarkable sensitivity towards the introduction of bulky substituents, which causes a changeover from a more associative to a more dissociative ring-closure process [19]. This effect almost disappears in the case of the significantly faster ring-closure reactions of the phen complexes, and must be related to the more structured, less flexible nature of this ligand than of bpy. The latter effect will cause the free end of the ligand to be closely associated, or even preassociated, with the Mo center, as was suggested in other studies [22–24]. This will cause a high local concentration of the "free" end of the potentially chelating ligand and account for the operation of an interchange (I) mechanism. It is also appropriate to think in terms of a 7-coordinate, 20 electron species in which the entering (phen) and leaving (CO) ligands are loosely coordinated either in the ground or in the transition state. The results of this study clearly show the importance of chelate rigidity in controlling the intimate mechanism for CO displacement during ring-closure reactions of metal carbonyl complexes.

Acknowledgments

The authors gratefully acknowledge financial support from the Department of Energy, Office of Basic Energy Science (EME) and the Deutsche Forschungsgemeinschaft (RvE).

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