

Mechanism of Thermal Ring Closure of $M(\text{CO})_5\text{L}$ (L = Bidentate Ligand) Produced during Photolysis of Group 6 Hexacarbonyl Complexes

K. Bal Reddy[†] and R. van Eldik*

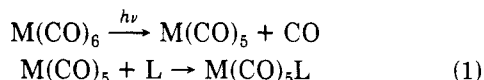
Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, FRG

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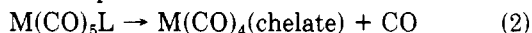
The kinetics of the thermal ring-closure reactions of $M(\text{CO})_5\text{L}$, produced during the photolysis of $M(\text{CO})_6/\text{L}$ for L = ethylenediamine (en) and 1,4-diisopropyl-1,4-diazabutadiene (dab), were studied as a function of [L], temperature, and pressure. The values of ΔS^\ddagger and ΔV^\ddagger are significantly negative, -40 to -170 J K⁻¹ mol⁻¹ and -5.4 to -13.7 cm³ mol⁻¹, respectively, for M = Cr (L = en) and M = Mo, W (L = en, dab) and support an associative ring-closure mechanism. For the Cr(CO)₅dab complex, the value of ΔV^\ddagger is significantly positive and is in line with a dissociative mechanism. The results demonstrate the crucial role played by the size of the metal center and the steric hindrance on L.

Introduction

The role of metal carbonyl complexes in mechanistic organometallic chemistry and in homogeneous catalytic processes has stimulated photochemical studies of such complexes.¹⁻⁴ The generation of intermediates has become a popular field of research. In this respect it is well-known that photolysis of $M(\text{CO})_6$ (M = Cr, Mo, W) results in the generation of $M(\text{CO})_5$, which can react with a ligand L to produce $M(\text{CO})_5\text{L}$ as indicated in (1).⁵ When L is a bi-



dentate ligand, the primary photolysis product $M(\text{CO})_5\text{L}$ will undergo a subsequent ring-closure reaction as shown in (2). This step has attracted much attention from



various investigators⁶⁻¹⁰ since it occurs over a wide time scale, ranging from milliseconds to several hours depending on the nature of the metal center and the bidentate ligand. In general the rate constant for such ring-closure reactions is independent of the concentration of L, and thermal activation parameters (especially ΔS^\ddagger) are used to assign the nature of the mechanism. Such data have indeed resulted in the assignment of specific mechanisms (associative or dissociative) for particular ring-closure reactions of $M(\text{CO})_5\text{L}$.^{6,11} Keeping in mind that mechanistic differentiation on the basis of relatively small differences in ΔS^\ddagger is subject to large uncertainty, we have suggested¹⁴ on the basis of our earlier experience to use pressure, and its associated activation parameter ΔV^\ddagger , as a mechanistic indicator.¹⁵⁻¹⁷ This technique has been applied with success in recent years to elucidate the substitution mechanisms of metal carbonyl complexes.¹⁸⁻²²

We have now investigated the pressure dependence of reaction 2 for M = Cr, Mo, W and L = ethylenediamine (en), 1,4-diisopropyl-1,4-diazabutadiene (dab). The results enable us to clearly differentiate between the associative and dissociative nature of the ring-closure reaction, which is controlled by the nature of both M and L.

Experimental Section

The parent hexacarbonyl complexes Cr(CO)₆ (Ventron), Mo(CO)₆ (Riedel-de-Haen), and W(CO)₆ (Riedel-de-Haen) were

further purified by sublimation under vacuum. Ethylenediamine (Merck) was distilled immediately prior to use. 1,4-Diisopropyl-1,4-diazabutadiene was prepared as described in the literature.⁶ Toluene (Merck, Uvasol) was refluxed over Na/K and distilled under nitrogen. Nitrogen used in the purging experiments was rigorously purified to remove H₂O and O₂ as described elsewhere.⁶ All handling of test solutions containing the metal carbonyl and ligand were carried out under an N₂ atmosphere with standard Schlenk techniques.

The kinetics of the thermal ring-closure reactions were followed spectrophotometrically on a modified (double-beam) Zeiss PMQ II Instrument incorporating a two-window thermostated (± 0.1 °C) high-pressure cell.^{23,24} In a typical experiment the deoxy-

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* To whom all correspondence should be addressed.

[†] On leave from the Department of Chemistry, Osmania University, Hyderabad 500007, India.

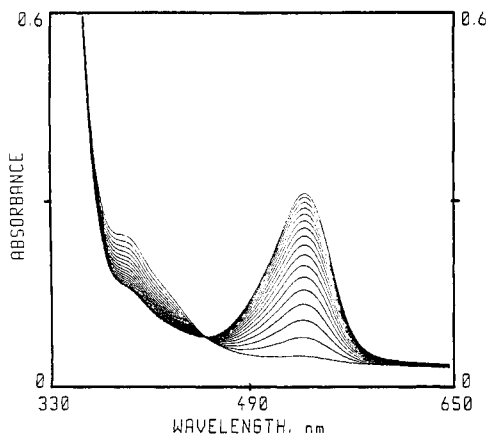


Figure 1. Repetitive-scan spectra for the reaction $\text{W}(\text{CO})_5\text{dab} \rightarrow \text{W}(\text{CO})_4\text{dab} + \text{CO}$. Conditions: $[\text{W}(\text{CO})_6] = 5 \times 10^{-4} \text{ M}$; $[\text{dab}] = 5 \times 10^{-3} \text{ M}$; temperature 40°C ; first spectrum recorded 5 min after 30-s irradiation of the $\text{W}(\text{CO})_6/\text{dab}$ mixture; subsequent spectra recorded at 45-min intervals.

generated solutions of $\text{M}(\text{CO})_6$ and L were mixed under N_2 and filled into a pillbox optical cell²⁵ with use of a specially designed filling system.²⁶ A small magnetic stirring bar was inserted into the pillbox cell prior to the test solution to enable effective stirring during irradiation with a 100-W high-pressure Hg lamp to produce the ring-opened $\text{M}(\text{CO})_5\text{L}$ complex. The subsequent thermal ring closure was followed in the instrument mentioned above for pressures up to 150 MPa. The temperature dependence study was performed in the thermostated ($\pm 0.1^\circ \text{C}$) cell compartment of a Shimadzu UV 250 spectrophotometer employing standard optical cells.

Results and Discussion

Irradiation of $\text{M}(\text{CO})_6$ in the presence of a bidentate ligand L produces the final ring-closed species $\text{M}(\text{CO})_4\text{L}$.⁵ This overall reaction involves the formation of $\text{M}(\text{CO})_5$ fragments and $\text{M}(\text{CO})_5\text{S}$ ($\text{S} = \text{solvent}$) and $\text{M}(\text{CO})_5\text{L}$ (ring-opened) species, of which the last is the final photolysis product. The existence of such species has been demonstrated with use of flash photolysis, rapid-scan, and conventional techniques.⁶⁻¹⁰ The relative stability of such $\text{M}(\text{CO})_5\text{L}$ transients depends on the nature of the metal center and the chelating ligand. The complexes selected in this study undergo subsequent ring closure on a relatively slow time scale such that conventional spectrophotometric techniques can be employed. Although many of these reactions were studied in benzene before, we preferred to use toluene as solvent since benzene freezes at relative low pressures (ca. 60 MPa at 25°C).

The ring-closure reactions can be followed conveniently by studying the increase in the characteristic MLCT band as a function of reaction time. Such spectral changes exhibit clean isosbestic points for at least 3 half-lives of the reaction as demonstrated by the example in Figure 1. The observed first-order rate constants were calculated in the usual way, and the corresponding plots were linear for at least 3 half-lives. No dependence of k_{obs} on either the ligand concentration (up to a 10-fold excess) or the slit width of the spectrophotometer was found, indicating that we are dealing with simple thermal ring-closure reactions, in agreement with earlier findings.⁶⁻⁸ For the $\text{M}(\text{CO})_6/\text{en}$ system it was observed that high en concentrations led to slow subsequent reactions that produced precipitates and resulted in some fluctuation in the value of k_{obs} . In order

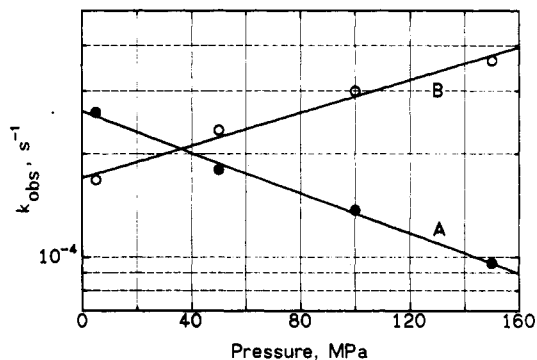


Figure 2. Plots of $\ln k_{\text{obs}}$ versus pressure for the reaction $\text{M}(\text{CO})_5\text{L} \rightarrow \text{M}(\text{CO})_4\text{L} + \text{CO}$. Conditions: $[\text{M}(\text{CO})_6] = 5 \times 10^{-4} \text{ M}$; $[\text{dab}] = 5 \times 10^{-3} \text{ M}$; $\text{M} = \text{Cr}$ (A), temperature 30°C ; $\text{M} = \text{W}$ (B), temperature 40°C .

to avoid this complication, the measurements in this study were performed for $[\text{M}(\text{CO})_6]:[\text{en}] = 1:1$. The observed rate constants for the investigated systems are summarized as a function of temperature and pressure in Table I. Plots of $\ln k_{\text{obs}}$ versus pressure are linear within experimental error limits, as demonstrated by two typical examples in Figure 2. The calculated activation parameters (ΔH^\ddagger , ΔS^\ddagger , and ΔV^\ddagger) are reported in Table I and summarized along with the available literature data for related systems in Table II.

A comparison of the rate constants for ring closure of $\text{M}(\text{CO})_5\text{L}$ for $\text{L} = \text{en}$, dab in Table I clearly demonstrates the significantly slower reaction in the case of the en complexes. This trend has been observed for other solvents before, and a reasonable explanation was offered.⁷ There are several factors such as ligand basicity, the ease of rotation around the carbon-carbon bond axis, and solvation effects on the uncoordinated nitrogen atom that cannot account for the stability of the $\text{M}(\text{CO})_5\text{en}$ species. Other factors such as the ability of the en ligand to rotate about the C-N bond and the sp^3 hybridization accounting for the tetrahedral environment surrounding the nitrogen atom will result in a substantial decrease in orbital angular overlap for the incoming nitrogen atom during ring closure and may account for the observed stability of the ring-opened species.⁷ In addition, rotation about the C-C bond in the dab ligand to attain the cis configuration is assisted by the steric interaction of the β -hydrogen atoms with CO in $\text{M}(\text{CO})_5\text{dab}$ and can account for the relatively rapid ring-closure reaction.⁶ The rate constants in Table II clearly demonstrate that ring closure on the en and dab complexes is significantly slower than for the bipyridine, diazafluorene, and pyridine-2-carbaldehyde imine ligands. The rate constants in Table I follow the sequence $\text{Mo} > \text{Cr} > \text{W}$ for both $\text{L} = \text{en}$ and $\text{L} = \text{dab}$, which is in agreement with that reported for the reactivity of the hexacarbonyls and the calculated M-C bond force constants of $\text{M}(\text{CO})_6$ in solution.²⁷ The observed rate constants are considerably greater than those reported for CO or L dissociation in $\text{M}(\text{CO})_5\text{L}$ in which the entering group is an amine, phosphine, or arsine ligand.²⁸ This increase is attributed to a substantial contribution toward the CO dissociation process when the associating ligand is already

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Table I. k_{obs} as a Function of Temperature and Pressure for the Reaction^a $\text{M}(\text{CO})_5\text{L} \rightarrow \text{M}(\text{CO})_4\text{L} + \text{CO}$

L	M	temp, °C	pressure, MPa	k_{obs} , ^b s ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹	ΔV^\ddagger , cm ³ mol ⁻¹
en	Cr	35	0.1	$(3.5 \pm 0.2) \times 10^{-5}$	57 ± 5	-145 ± 17	
		40		$(5.6 \pm 0.1) \times 10^{-5}$			
		45		$(8.9 \pm 0.1) \times 10^{-5}$			
		50		$(9.2 \pm 0.4) \times 10^{-5}$			
		55		$(15.5 \pm 0.2) \times 10^{-5}$			
	Mo	35	0.1	$(6.6 \pm 0.5) \times 10^{-5}$	72 ± 7	-92 ± 22	
		40		$(12.5 \pm 0.5) \times 10^{-5}$			
		45		$(17.0 \pm 0.7) \times 10^{-5}$			
		50		$(26.7 \pm 0.5) \times 10^{-5}$			
		40		$(13.7 \pm 0.7) \times 10^{-5}$			
	W	45	0.1	$(9.6 \pm 0.1) \times 10^{-6}$	54 ± 5	-172 ± 16	
		50		$(15.2 \pm 0.2) \times 10^{-6}$			
		55		$(19.4 \pm 0.9) \times 10^{-6}$			
		60		$(25.7 \pm 0.7) \times 10^{-6}$			
		50		$(15.5 \pm 0.6) \times 10^{-6}$			
dab	Cr	15	0.1	$(4.5 \pm 0.2) \times 10^{-5}$	81 ± 2	-47 ± 7	
		25		$(1.52 \pm 0.05) \times 10^{-4}$			
		30		$(2.6 \pm 0.1) \times 10^{-4}$			
		35		$(4.2 \pm 0.1) \times 10^{-4}$			
		30		$(2.6 \pm 0.2) \times 10^{-4}$			
	Mo	15	0.1	$(2.85 \pm 0.02) \times 10^{-4}$	78 ± 5	-40 ± 17	
		25		$(1.11 \pm 0.04) \times 10^{-3}$			
		35		$(2.9 \pm 0.2) \times 10^{-3}$			
		40		$(4.2 \pm 0.6) \times 10^{-3}$			
		25		$(1.07 \pm 0.03) \times 10^{-3}$			
	W	20	0.1	$(1.6 \pm 0.2) \times 10^{-5}$	83 ± 8	-53 ± 26	
		30		$(4.6 \pm 0.2) \times 10^{-5}$			
		35		$(7.3 \pm 0.3) \times 10^{-5}$			
		40		$(1.6 \pm 0.2) \times 10^{-4}$			
		40		$(1.68 \pm 0.02) \times 10^{-4}$			
				$(2.32 \pm 0.09) \times 10^{-4}$		-13.7 ± 1.3	
				$(2.99 \pm 0.03) \times 10^{-4}$			
				$(3.63 \pm 0.06) \times 10^{-4}$			
				$(1.8 \pm 0.1) \times 10^{-4}$			
				$(1.37 \pm 0.09) \times 10^{-4}$			
				$(0.96 \pm 0.03) \times 10^{-4}$		$+17.2 \pm 1.0$	
				$(1.8 \pm 0.1) \times 10^{-4}$			
				$(1.31 \pm 0.08) \times 10^{-3}$			
				$(1.52 \pm 0.04) \times 10^{-3}$			
				$(1.89 \pm 0.07) \times 10^{-3}$			

^a Experimental conditions: solvent toluene; $[\text{M}(\text{CO})_6] = 5 \times 10^{-4}$ M for [dab] = 5×10^{-3} M; $[\text{M}(\text{CO})_6] = 7.5 \times 10^{-4}$ M for [en] = 7.5×10^{-4} M. ^b Mean value of at least three kinetic runs.

attached to the metal center in a monodentate fashion, as is the case during the studied ring-closure reactions.

The activation parameters in Table I demonstrate that ΔH^\ddagger is significantly smaller for the ring closure of the en complexes (M = Cr, W) than for the dab complexes. The significantly more negative values of ΔS^\ddagger account for the overall smaller rate constants for L = en. This comparison can be extended to the ring-closure reactions of similar pentacarbonyl complexes summarized in Table II. In most cases ΔS^\ddagger is significantly negative, in line with an associative ring-closure process, and only a few exceptions are present. In these cases ΔS^\ddagger is close to zero and its mechanistic meaning is questionable. In general the ΔH^\ddagger values are significantly lower than those reported for the dissociation of CO in $\text{M}(\text{CO})_6$, viz. 159–167 (M = Cr), 125–134 (M = Mo), and 163–167 kJ mol⁻¹ (M = W),^{29–31}

which may be due to the cis-labilization effect of the monodentate en ligand and its tendency to ring-close associatively once it is bonded in this way. This further underlines the possible operation of an associative ring-closure mechanism. However, there is a clear exception, viz. the ring closure of $\text{Cr}(\text{CO})_5\text{dab}$, for which ΔV^\ddagger is significantly positive.

In general the ΔS^\ddagger and ΔV^\ddagger values in Table I exhibit very similar trends. The significantly negative ΔV^\ddagger values observed for the majority of the reactions underline the operation of an associative mechanism. ΔV^\ddagger is significantly positive in the case of the $\text{Cr}(\text{CO})_5\text{dab}$ system, indicating that ring closure proceeds via the dissociation of CO. The value of $+17.2 \pm 1.0$ cm³ mol⁻¹ is in close agreement with

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Table II. Summary of Rate and Activation Parameters for Ring-Closure Reactions of $M(\text{CO})_5\text{L}$

M	L ^a	solvent	$k(25^\circ\text{C})$, ^b s ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹	ΔV^\ddagger , cm ³ mol ⁻¹	ref	
Cr	daf	benzene	1.4×10^{-3}	80 ± 5	-31 ± 19		11	
	pyc, R = <i>t</i> -C ₄ H ₉		8.3×10^{-6}	86 ± 5	-32 ± 8		12	
	dab, R = <i>t</i> -C ₄ H ₉		4.6×10^{-3}	70 ± 5	-53 ± 33		13	
	dab, R = C ₆ H ₁₁		2.2×10^{-4}	73 ± 8	-70 ± 17		6	
	dab, R = C ₃ H ₇		2.1×10^{-4}	80 ± 8	-47 ± 17		6	
	dab, R = C ₄ H ₉		4.0×10^{-3}	68 ± 8	-60 ± 17		6	
	en		C ₆ H ₅ CH ₃	1.6×10^{-5}	57 ± 5	-145 ± 17	-11.9 ± 1.5	7, c
	dab, R = <i>i</i> -C ₃ H ₇			1.5×10^{-4}	81 ± 2	-47 ± 7	$+17.2 \pm 1.0$	c
Mo	daf	benzene	1.5×10^{-1}	90 ± 6	$+43 \pm 21$		11	
	pyc, R = <i>t</i> -C ₄ H ₉		3.8×10^{-3}	45 ± 8	-141 ± 16		12	
	dab, R = <i>t</i> -C ₄ H ₉		1.3×10^{-2}	85 ± 5	$+5 \pm 33$		13	
	dab, R = C ₆ H ₁₁		1.0×10^{-2}	70 ± 8	-68 ± 17		6	
	dab, R = C ₃ H ₇		1.3×10^{-3}	77 ± 8	-42 ± 17		6	
	dab, R = C ₄ H ₉		1.3×10^{-2}	83 ± 8	$+2 \pm 17$		6	
	dab, R = C ₈ H ₉		6.6×10^{-3}	65 ± 8	-68 ± 17		6	
	en		C ₆ H ₅ CH ₃	3.0×10^{-5}	72 ± 7	-92 ± 22	-5.4 ± 0.8	7, c
dab, R = <i>i</i> -C ₃ H ₇	1.1×10^{-3}	78 ± 5		-40 ± 17	-9.5 ± 0.4	c		
W	daf	benzene	1.4×10^{-4}	88 ± 6	-23 ± 21		11	
	pyc, R = <i>t</i> -C ₄ H ₉		2.3×10^{-5}	82 ± 8	-57 ± 12		12	
	pyc, R = C ₆ H ₅		3.0×10^{-3}	46 ± 8	-140 ± 16		12	
	pyc, R = <i>i</i> -C ₃ H ₇		3.7×10^{-3}	57 ± 7	-98 ± 14		12	
	pyc, R = <i>n</i> -C ₄ H ₉		1.9×10^{-2}	27 ± 8	-179 ± 18		12	
	dab, R = <i>t</i> -C ₄ H ₉		1.0×10^{-4}	82 ± 5	-44 ± 33		13	
	bpy		6.8×10^{-2}	80 ± 8	$+2 \pm 16$		6	
	bpy, R = CH ₃		5.7×10^{-2}	69 ± 8	-38 ± 16		6	
	bpy, R = C ₄ H ₉		3.2×10^{-2}	71 ± 8	-36 ± 16		6	
	bpy, R = C ₆ H ₅		3.2×10^{-2}	67 ± 8	-48 ± 16		6	
	dab, R = C ₆ H ₁₁		6.9×10^{-5}	80 ± 8	-54 ± 16		6	
	dab, R = C ₃ H ₇		3.3×10^{-5}	87 ± 8	-37 ± 16		6	
	dab, R = C ₄ H ₉		1.4×10^{-5}	80 ± 8	-52 ± 16		6	
	dab, R = C ₈ H ₉		1.1×10^{-4}	103 ± 8	$+26 \pm 16$		6	
	en		C ₆ H ₅ CH ₃	3.0×10^{-6}	54 ± 5	-172 ± 16	-12.3 ± 1.4	7, c
	dab, R = <i>i</i> -C ₃ H ₇			2.9×10^{-5}	83 ± 8	-53 ± 26	-13.7 ± 1.3	c
bpy		8.0×10^{-2}	58 ± 2	-74 ± 7	-10.9 ± 1.1	14		

^a The following abbreviations are used: daf = 4,5-diazafluorene; pyc = pyridine-2-carbaldehyde imine; dab = 1,4-diaza-1,4-butadiene; bpy = 2,2'-bipyridine. ^b Experimental or extrapolated (from quoted activation parameters) values. ^c This work.

that reported for the dissociation of CO from $\text{HRu}_3(\text{CO})_{11}^-$ ($+21.2 \pm 1.4$),¹⁹ $\text{Ru}_3(\text{CO})_{10}(\text{P}(\text{OMe})_3)(\text{CO}_2\text{Me})^-$ ($+24 \pm 2$),¹⁹ and $\text{Mn}(\text{CO})_5\text{Cl}$ ($+20.6 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$),²¹ for which a limiting D mechanism was suggested. The changeover in mechanism observed for the ring closure of $\text{Cr}(\text{CO})_5\text{en}$ and $\text{Cr}(\text{CO})_5\text{dab}$ is presumably due to the steric hindrance by the isopropyl substituents on the dab ligand. In the case of the larger Mo and W metal centers, ring closure of the dab complex is not affected by the steric hindrance and an associative reaction mode is operative. In this respect it is interesting to note that the ring-closure reactions of $\text{M}(\text{CO})_5\text{phen}$ (M = Cr, Mo, W and phen = 1,10-phenanthroline) also exhibit the same trend in their associated ΔV^\ddagger values as reported for the dab complex here.³² Such a mechanistic changeover caused by steric hindrance on a chelate ligand was also observed for substitution re-

actions of complexes of the type $\text{M}(\text{CO})_4(\text{SS})$ for M = Cr and Mo.²² Furthermore, the size of the central metal atom also plays a prominent role in the substitution behavior of complexes of the type $\text{M}(\text{CO})_5(\text{solvent})$ for M = Cr, Mo, W.³³

We conclude that the reported volumes of activation for thermal ring-closure reactions of complexes of the type $\text{M}(\text{CO})_5\text{L}$, where L is a bidentate ligand, greatly assist the assignment of the intimate mechanism of this process. Especially in systems where ΔS^\ddagger provides no definite mechanistic information it will be essential to measure ΔV^\ddagger in order to draw meaningful mechanistic conclusions.

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