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Can Steric Hindrance Cause a Gradual Change in the Ring-Closure Mechanism of Complexes of the Type $W(CO)_5N$-N, Where N-N Represents a Series of Substituted Bipyridine Ligands?

Shibai Cao, Kedika Bal Reddy, Edward M. Eyring,* and Rudi van Eldik[1]

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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The kinetics of the thermal ring-closure reactions of $W(CO)_5L$, produced during the photolysis of $W(CO)_6/L$, where L = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 4,4′-diphenyl-2,2′-bipyridine and 4,4′-di-*tert*-butyl-2,2′-bipyridine, were studied as a function of pressure. The values of the activation parameter $\Delta V^\ddagger$ are small and negative for these ligands, supporting an associative interchange mechanism (I_a) for CO extrusion. The $\Delta V^\ddagger$ values exhibit a specific trend toward more positive values on increasing the steric hindrance on the ligand. This trend is interpreted as evidence for a gradual change in mechanism from a more associative to a more dissociative ring-closure process.

Introduction

Recent kinetic studies have revealed the sensitivity of ligand substitution reactions of group 6 carbonyl complexes to the size of the central metal atom.[2–10] Solvent displacement reactions of complexes of the type $M(CO)_5S$ indicate a distinct trend along the series M = Cr, Mo, and W, in which bond formation becomes more important for the larger members of the metal series.[2–5] A similar trend was reported for ring-closure reactions of complexes of the type $M(CO)_5N$-N, where N-N = 1,4-diisopropyl-1,4-diazabutadiene and 1,10-phenanthroline, in which the smallest metal center Cr first undergoes loss of CO prior to ring closure, whereas the larger metal centers Mo and W follow an associative ring-closure mechanism.[6,7] In the case of the bulky phenanthroline ligand, it was observed that the Mo complexes may be representative of an intermediate case in which an interchange mechanism is operative. Clearly, these studies demonstrated the sensitivity of the mechanism to the size of the central metal atom. An aspect of this reaction that warranted further study is the effect of steric hindrance on the entering ligand and the extent to which this could affect the nature of the ring-closure mechanism in complexes of the type $M(CO)_5N$-N. Naturally, the largest sensitivity would be expected for the metal center of intermediate size, viz. Mo. In fact, a detailed study of such ring-closure reactions for a series of substituted 2,2′-bipyridine and substituted 1,10-phenanthroline complexes showed a gradual change in mechanism from more associative to more dissociative with increasing bulkiness of the substituents on the chelate, i.e., on increasing steric hindrance on the N donor atom.[9,10]

The question that remains is whether such a gradual change is also possible for the largest metal center of the series, viz. W. We have therefore undertaken a systematic study of the ring-closure reactions of a series of substituted bipyridine complexes of $W(CO)_5N$-N. These species were prepared in situ via the flash photolysis of $W(CO)_6$ in the presence of the bipyridine ligands. We used, as in our earlier work,[2–10] high-pressure kinetic techniques to resolve the nature of the subsequent thermal ring-closure reaction. The volume of activation that can be obtained from such data has been shown to be a very sensitive and reliable mechanistic indicator.[11,12]

Experimental Section

$W(CO)_6$ (Aldrich) was vacuum-sublimed before use. 2,2′-Bipyridine (bpy) (Aldrich) and 4,4′-dimethyl-2,2′-bipyridine (dmbpy) (Aldrich) were used without further purification. Technical grade 4,4′-diphenyl-2,2′-bipyridine (dpbpy) (Aldrich) was recrystallized twice from toluene. 4,4′-Di-*tert*-butyl-2,2′-bipyridine (dbubpy) was prepared according to a literature procedure for the ortho dehydration of pyridine derivatives over Raney Nickel.[13] Toluene (Aldrich) was distilled over Na under a nitrogen atmosphere. All test solutions were prepared under a N_2 atmosphere using Schlenk techniques. The photolysis beam for the pulsed laser flash photolysis studies was from a Quanta-Ray DCR-2 Nd:YAG laser operating at 10 Hz and λ = 355 nm (100 mJ/pulse, 5–6-ns fwhi). The system employed an Oriel 75-W xenon lamp as the analyzing source, a Durrum monochromator, and a Hamamatsu 1P28 photomutiplier detector. The photolysis beam intersected the observation beam at right angles in the high-pressure spectrophotometric cell.[14] The high-pressure cell was equipped with a thermostating coil (±0.1 °C) and was pressurized with heptane up to 150 MPa. A mechanical hydraulic

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[1] On leave from the Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Str. 10, 58448 Witten, Germany.

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pump (heptane) was used for this purpose. A quartz pillbox sample cell[16] with an optical path length of ca. 15 mm was used as the observation cell. Solutions were introduced into the cell with a special filling system.[16] The signal was sent to the LeCroy 9400 oscilloscope interfaced (GPIB) to an IBM-compatible PC (Zenith). Data were analyzed using KINFIT software purchased from OLIS. The first-order rate constants, k_{obs}, were obtained by averaging 5–15 kinetic traces. Volumes of activation were determined from the slopes ($-\Delta V^{\ddagger}/RT$) of the plots of ln k_{obs} versus pressure, which were all linear within the experimental error limits over the investigated pressure range.

Results and Discussion

Irradiation of a mixture of $M(CO)_6$ and a variety of ligands rapidly produces $M(CO)_5L$ (L = a bidentate ligand), where L is coordinated in a monodentate fashion.[17] This is followed by a slow thermal ring-closure reaction leading to the tetracarbonyl complex and the release of CO as shown in eq 2. The existence of the ring-opened

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO$$

$$M(CO)_5 + solv \xrightarrow{fast} M(CO)_5\ solv$$

$$M(CO)_5\ solv + L \xrightarrow{k_1} M(CO)_5L + solv \qquad (1)$$

$$M(CO)_5L \xrightarrow{k_2} M(CO)_4L + CO \qquad (2)$$

$M(CO)_5$ L species has been convincingly demonstrated earlier using a diode-array spectrophotometer and conventional techniques.[18–22] In general, reaction 1 is characterized by a linear dependence of k_{obs} on the concentration of L, whereas the subsequent ring-closure reaction (2) exhibits first-order kinetics independent of the concentration of L. The relative stability of $M(CO)_5L$ depends on the nature of the metal center and the chelating ligand. Earlier studies[18–23] were carried out in benzene as solvent, but since benzene freezes at approximately 75 MPa at 25 °C, we preferred in the present study to use toluene as the solvent. Experience has shown that the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ usually reveal limited mechanistic information in such reactions, and in general much uncertainty exists in the interpretation of $\Delta S^{\ddagger}$ data.[20–22,24] In our experience the application of pressure as a kinetic parameter can reveal very reliable mechanistic information, thus facilitating the assignment of the underlying reaction mechanism.[25–27] It is always good practice to have as much information as possible in support of a proposed mechanism, including $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$ values. The low oxidation states of these complexes and the use of neutral ligands simplify the interpretation of the observed pressure effects, since these effects can, in the absence of major solvational changes, be associated with intrinsic volume changes arising from changes in bond lengths and bond angles during the substitution process.[28]

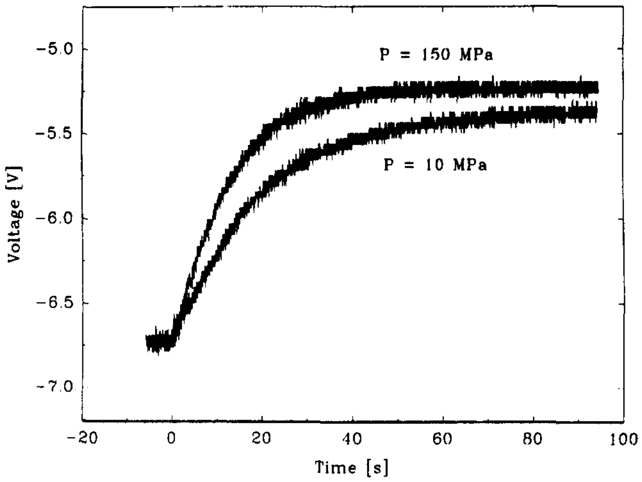

Figure 1. Typical kinetic traces recorded for the ring-closure reaction $W(CO)_5dmbpy \rightarrow W(CO)_4dmbpy + CO$. Experimental conditions: $[W(CO)_6] = 2 \times 10^{-3}$ M; $[L] = 2 \times 10^{-2}$ M; wavelength = 506 nm; $T = 25.0$ °C. Vertical axis represents relative absorbance for which −10 V equals 100% transmission.

The carbonyl extrusion from $W(CO)_5L$ generated by laser flash photolysis was monitored by an increase in absorbance at the characteristic MLCT band of the $W(CO)_4L$ complex. Figure 1 shows typical kinetic traces recorded at 506 nm following the laser flash at two different pressures. k_{obs} was found to be independent of the concentration of L over at least a 10-fold concentration range. Thus the chelate ring-closure reaction obeys the rate law (3), where k_2 is the rate constant for chelate ring

$$-d[W(CO)_5L]/dt = k_2[W(CO)_5L] \qquad (3)$$

closure. Rate constants were measured as a function of pressure for different ligands L and are presented along with activation volume data in Table 1. Plots of ln k_2 versus pressure were linear within the experimental error limits of between 3 and 10% in all cases.

It is immediately apparent from the kinetic data that the ring-closure reaction rate depends strongly on the nature of the bipyridine ligand. The rate of ring closure of $W(CO)_5L$ complexes follows the order bpy > dmbpy > dpbpy > dbubpy, in agreement with that found in an earlier study.[20] Thus an increase in steric hindrance on the chelating ligand does significantly affect the rate of ring closure. The $\Delta V^{\ddagger}$ values are small and negative for these ligands, supporting an associative interchange mechanism (I_a) for CO extrusion.[27] The introduction of two methyl substituents causes an increase in $\Delta V^{\ddagger}$ of almost 2.5 cm^3 mol^{-1}, whereas the introduction of two phenyl and two *tert*-butyl substituents causes an increase in $\Delta V^{\ddagger}$ of 4.5 and 6.4 cm^3 mol^{-1}, respectively. The $\Delta V^{\ddagger}$ values exhibit a specific trend toward more positive values with increasing steric hindrance on the ligand, which is interpreted as evidence for a gradual change in mechanism from a more associative to a more dissociative ring-closure process. There is no change in the sign of the $\Delta V^{\ddagger}$, which indicates that bond formation is always the dominating process.

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Table 1. Rate Constants and Activation Volumes for Chelate Ring Closure in $W(CO)_5L$ Complexes in Toluene[a]

L	P, MPa	k_{obs},[b] s^{-1}	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$
bpy[c]	5	0.080 ± 0.002	−10.9 ± 1.1
(514 nm)	25	0.091 ± 0.003	
	50	0.105 ± 0.003	
	75	0.113 ± 0.002	
	100	0.122 ± 0.004	
dmbpy	10	0.048 ± 0.003	−8.4 ± 1.0
(506 nm)	50	0.059 ± 0.001	
	100	0.068 ± 0.001	
	150	0.078 ± 0.002	
dpbpy	10	0.034 ± 0.003	−6.4 ± 0.6
(534 nm)	50	0.038 ± 0.002	
	100	0.045 ± 0.003	
	150	0.049 ± 0.004	
dbubpy	10	0.023 ± 0.003	−4.5 ± 0.2
(502 nm)	50	0.025 ± 0.001	
	100	0.027 ± 0.001	
	150	0.030 ± 0.001	

[a] Experimental conditions: $[W(CO)_6] = 2 \times 10^{-3}$ M; $[L] = 2 \times 10^{-2}$ M; $T = 25.0$ °C. Wavelengths of MLCT bands of the $W(CO)_4L$ complexes where reactions were followed are given in parentheses. [b] Mean value of 5–15 kinetic runs. [c] Reference 30.

Table 2. Activation Volumes for Chelate Ring Closure in $M(CO)_5L$ Complexes in Toluene (M = Mo, W)

L	M	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$	ref
bpy	Mo	−3.9 ± 0.6	9
	W	−10.9 ± 1.1	30
dmbpy	Mo	−5.6 ± 0.4	9
	W	−8.4 ± 1.0	*a*
dpbpy	Mo	5.4 ± 0.5	9
	W	−6.4 ± 0.6	*a*
dbubpy	Mo	6.2 ± 1.0	*b*
	W	−4.5 ± 0.2	*a*

[a] This work. [b] In order to complete this comparison, the same reaction was studied for $Mo(CO)_6$. Experimental conditions: $[Mo(CO)_6] = 2 \times 10^{-3}$ M; $[L] = 2 \times 10^{-2}$ M; $T = 25.0$ °C. The k_{obs} values were 1.84 ± 0.03, 1.55 ± 0.09, 1.43 ± 0.05, and 1.29 ± 0.05 s^{-1}, at 10, 50, 100, and 150 MPa, respectively.

Table 3. Summary of the Activation Volumes for Ring-Closure Reactions of $W(CO)_5L$ Complexes[a]

solvent	L	k_2(25 °C), s^{-1}	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$	ref
Tol	en	3.0×10^{-6}	−12.3 ± 1.4	6
Tol	dabR_2	2.9×10^{-5}	−13.7 ± 1.3	6
Tol	dbubpy	2.3×10^{-2}	−4.5 ± 0.2	*b*
Tol	dpbpy	3.4×10^{-2}	−6.4 ± 0.6	*b*
Tol	dmbpy	4.8×10^{-2}	−8.4 ± 1.0	*b*
Tol	bpy	8.0×10^{-2}	−10.9 ± 1.1	30
Tol	phen	4.3×10^{2}	−8.2 ± 0.2	7

[a] Abbreviations used: Tol = toluene, en = ethylenediamine, dabR_2 = 1,4-diisopropyl-1,4-diazabutadiene, phen = 1,10-phenanthroline. [b] This work.

However, considerable extrusion of coordinated CO must occur during ring closure of the sterically more hindered chelates to account for the significant increase in $\Delta V^{\ddagger}$.

A comparison of the data in Table 2 indicates that the $\Delta V^{\ddagger}$ values for the similar ring-closure reactions of $Mo(CO)_5L$ strongly suggest a gradual change in mechanism from I_a to I_d on increasing the steric hindrance on the bpy ligand.[9] Only in the case of the most sterically hindered dpbpy and dbubpy complexes does a change in sign of $\Delta V^{\ddagger}$ really occur; i.e., in this case the steric hindrance reaches a critical point where an associative (I_a) ring closure is no longer possible, and the reaction is forced to follow a dissociative (I_d) mechanism. A similar changeover in mechanism caused by steric hindrance was observed for ligand substitution reactions of $(S_2)Mo(CO)_4$ (S_2 = 2,5-dithioalkane) complexes.[29] In the case of the larger W metal center, the data in Table 2 indicate that the mechanism of the ring-closure reaction of substituted bpy complexes is only slightly affected by the steric hindrance on the bpy ligand, and an associative reaction mode is operative in all cases. The $\Delta V^{\ddagger}$ data for the W complexes are between 7 and 11 $cm^3\ mol^{-1}$ more negative than those for the corresponding Mo complexes, which indicates that the larger W metal center has a greater ability to undergo bond formation with the ring-opened chelate. Clearly, these studies demonstrate the sensitivity of the ring-closure mechanism to the size of the central metal atom and to the effect of the steric hindrance on the entering ligand.

A summary of the available rate and activation volume data for ring-closure reactions of $W(CO)_5L$ complexes is given in Table 3. The systems have been ordered according to increasing k_2 values, demonstrating the ease of ring closure for the more structured chelating ligands. The data indicate that k_2 for the investigated bipyridine systems is significantly larger than that for en and dabR_2 but significantly smaller than that for the phen complex. The latter trend is related to the rigidity of the phen ligand that causes intramolecular interactions between the uncoordinated site of the phen ligand and the W center in the ring-opened species.[7] The $\Delta V^{\ddagger}$ values are all negative, which indicates that the ring closure of $W(CO)_5L$ mainly proceeds via an associative interchange (I_a) mode due to the larger size of the W metal center. The results indicate that a gradual change in mechanism resulting from changing the steric hindrance on the entering ligands is more difficult to accomplish for the larger W metal center than for the Mo metal center.

We conclude that the size of both the metal center and the structure of the coordinated ligand play a crucial role in determining the location of the transition state along the reaction coordinate for the ring-closure reaction, which involves bond cleavage with the leaving group and bond formation with the entering nucleophile. We are convinced that the experimental values of $\Delta V^{\ddagger}$ greatly facilitate the assignment of the intimate nature of the ligand substitution process.[11]

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