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Thermal Ring-Closure Reactions of Pentacarbonylchromium Complexes with Bidentate N−N Ligands Revisited. Elimination of Side Reactions and Elucidation of the Intimate Chelation Mechanism

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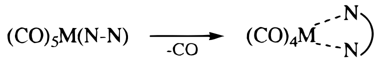
Thermal ring-closure reactions of pentacarbonylmetal complexes with bidentate N−N ligands were studied in detail in the past using photochemical techniques to produce these species in solution prior to the actual reaction. Some of the monodentate pentacarbonylchromium complexes have now been isolated and enable a detailed reinvestigation of the thermal chelation reaction of $Cr(CO)_5(N-N)$ (N−N = 1,4-diisopropyl-1,4-diazabutadiene, 4,4′-dimethyl-2,2′-bipyridine). The reactions were studied as a function of [N−N], temperature, and pressure. The unexpected ligand concentration dependence, viz. a decrease in observed rate constant with increasing [N−N], can be accounted for in terms of competitive reactions leading to the formation of $Cr(CO)_6$ and chelated $Cr(CO)_4(N-N)$. At high [N−N] the limiting rate constant represents only the chelation reaction, for which the observed activation volumes are between +13 and +18 $cm^3\ mol^{-1}$. These strongly support the operation of a dissociatively activated chelation mechanism.

Introduction

Recent kinetic studies on the thermal ring closure reactions of complexes of the type $M(CO)_5L$ (M = Cr, Mo, W; L = bidentate ligand) indicated that the mechanism of such processes is controlled to a large extent by the size of the metal center and the nature of the chelating ligand.[1−16] In these investigations the $M(CO)_5L$ species were prepared in solution by photolysis of $M(CO)_6$ in the presence of L. The reaction involves the initial photodissociation of one CO ligand (eq 1), leading to the intermediate pentacarbonyl with a monocoordinated bidentate ligand (eq 2), which subsequently undergoes ring closure by loss of another CO (eq 3). If reaction 3 is too rapid, it is necessary to use flash photolysis techniques in order to study its kinetics.[9,12−15]

$$M(CO)_6 \xrightarrow[-CO]{h\nu} M(CO)_5 \qquad (1)$$

$$M(CO)_5 + N\text{-}N \longrightarrow (CO)_5M(N\text{-}N) \qquad (2)$$


(3)

The intimate nature of the ring-closure process was especially revealed by the more recently reported volumes of activation.[11−14] It could be demonstrated that the volume of activation is the best parameter to describe the nature of the different ring-closure mechanisms. The pressure dependence of these reactions was usually studied under conditions similar to those adopted for the ambient-pressure studies.[3−6,8,16] In fact for L = phen, en (ethylenediamine), and dab (1,4-diisopropyl-1,4-diazabutadiene), the volumes of activation for M = Mo and W were all significantly negative and supported the operation of an associatively activated chelation mechanism.[9,11−14] For M = Cr, however, the volume of activation suggested a fine balance between the size of the metal center and steric hindrance on the free end of the bidentate ligand as the transition state is approached,[11] which controlled the intimate nature of the chelation mechanism in terms of an associative or dissociative process.

It is in this respect that recent reports in the literature, dealing with the isolation and chelation

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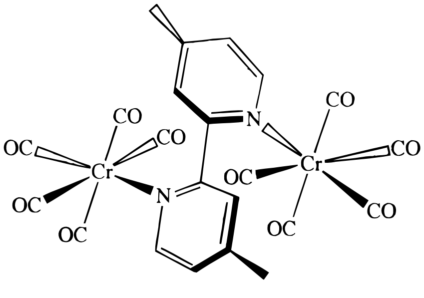
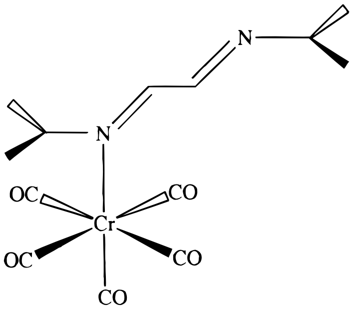
reactions of $(CO)_5Cr(\mu\text{-dmbpy})Cr(CO)_5$ and $(CO)_5Cr(dab)$, where dmbpy = 4,4′-dimethyl-2,2′-bipyridine, attracted our attention.[17−19] These complexes undergo thermal chelation reactions to produce the chelated tetracarbonyl species via rate-determining extrusion of CO. The authors concluded that these species simulate the intermediates produced in the photoinduced reactions and exhibit properties different from those found before. In this respect, significant formation of $Cr(CO)_6$ was found at low dmbpy and dab concentrations.[17−19] Furthermore, the bridged complex was isolated at low $Cr(CO)_5$ to dmbpy concentration ratios, which immediately raised the question to what extent such bridged species could have occurred in our earlier photoinduced studies and, if they did, how they would have affected the observed kinetic behavior.


$Cr(CO)_5(\mu\text{-dmbpy})Cr(CO)_5$


$Cr(CO)_5(dab)$

We have therefore undertaken a detailed kinetic study of the chelate formation reaction (eq 3) for both the bridging dmbpy and dab complexes. These results clearly show that the concentration of the free bidentate ligand in solution controls the extent of chelate product formation. The reported activation parameters determined under limiting concentration conditions are all in favor of a dissociatively activated chelation reaction.

Experimental Section

Chromium hexacarbonyl and 4,4′-dimethyl-2,2′-bipyridine (dmbpy) were purchased from Aldrich and used as received. The complexes were prepared from $Cr(CO)_5(\eta^2\text{-}(Z)\text{-cyclooctene})$ and dab or dmbpy according to the published procedures.[18−20] Important to note is the fact that we used considerably more solvent (pentane) in the preparation of the bridged complex than was mentioned in the literature due to the limited solubility of dmbpy. The products were characterized by IR and elemental analysis, and the results were in good agreement with those reported in the literature.[18] Toluene (Merck, Roth) and hexane (Aldrich) were of spectroscopic grade, refluxed over Na/K and distilled under nitrogen or argon. All manipulations involving the test solutions were carried out under an argon or nitrogen atmosphere in the dark using standard Schlenk techniques. Kinetic data for the chelation reaction at ambient pressure were obtained using a Varian Cary 1.3 or a HP8452A diode array spectrophotometer ($\epsilon(Cr(CO)_5(\mu\text{-dmbpy})Cr(CO)_5$ (410 nm)) = 5150 L mol^{-1} cm^{-1};[18] $\epsilon(Cr(CO)_4$dmbpy (518 nm)) = 3100 L mol^{-1} cm^{-1}; $\epsilon(Cr(CO)_5$-dab (405 nm)) = 4450 L mol^{-1} cm^{-1} and $\epsilon(Cr(CO)_4$dab (586 nm)) = 8140 L mol^{-1} cm^{-1}).[19] The kinetics at elevated pressure were followed on a modified Varian Cary 1.3 UV−vis spectrophotometer equipped with a thermostated high-pressure cell.[21,22] The deoxygenated solutions were introduced into the optical pill-box cell[23] under an argon or nitrogen atmosphere by using a specially designed filling system.[24]

Mononuclear ring-opened $Cr(CO)_5(dmbpy)$, i.e., the compound in which only one nitrogen donor of dmbpy is coordinated, was also produced photochemically in solution by irradiation of 5×10^{-4} M $Cr(CO)_6$ and dmbpy (6.25−100 mM) in toluene for 20 s using a 100 W high-pressure Hg lamp, similar to the experiments performed for $Cr(CO)_6$ and dab before.[12] The subsequent thermal ring-closure reaction of the complex at high ligand concentrations was followed by the growth of the MLCT band of $Cr(CO)_4(dmbpy)$ at 518 nm. The formation of $Cr(CO)_4(dab)$ was followed at 586 nm using the isolated $Cr(CO)_5(dab)$ as starting material. The kinetic traces were fitted with the OLIS-KINFIT set of programs.[25] Calculation of the volumes of activation was performed in the usual way, and plots of ln k_{obs} vs pressure were linear within the experimental error limits. Immediately following the chelation reaction, an IR spectrum of the product solution was recorded with a Nicolet FX5 FT-IR spectrophotometer in a 1 mm pathway NaBr cell to confirm the approximate composition of the product mixtures generated during the thermal process. From the IR spectra it followed qualitatively that in the case of using a high ligand concentration nearly no formation of $Cr(CO)_6$ could be observed. However, at low ligand concentration (or when no ligand was added) we observed a strong signal at 1987 cm^{-1} due to the formation of $Cr(CO)_6$. For the experiments in the presence of CO, we used the highest available quality (99.97% Linde).

Results and Discussion

A. Thermal Behavior of $Cr(CO)_5(\mu\text{-dmbpy})Cr(CO)_5$. The spectral changes observed in the UV−vis region during the transformation of the title complex in toluene into the respective products were recorded as a function of dmbpy concentration, temperature, and pressure. The observed spectral changes (Figure 1a) are in agreement with those reported before and clearly demonstrate that the extent of chelate product formation, i.e., $Cr(CO)_4(dmbpy)$, depends strongly on the dmbpy concentration employed.[18] At low dmbpy concentration (Figure 1b) almost no conversion to $Cr(CO)_4(dmbpy)$ occurs and the main product is $Cr(CO)_6$, as confirmed by IR spectroscopy of the reaction products.

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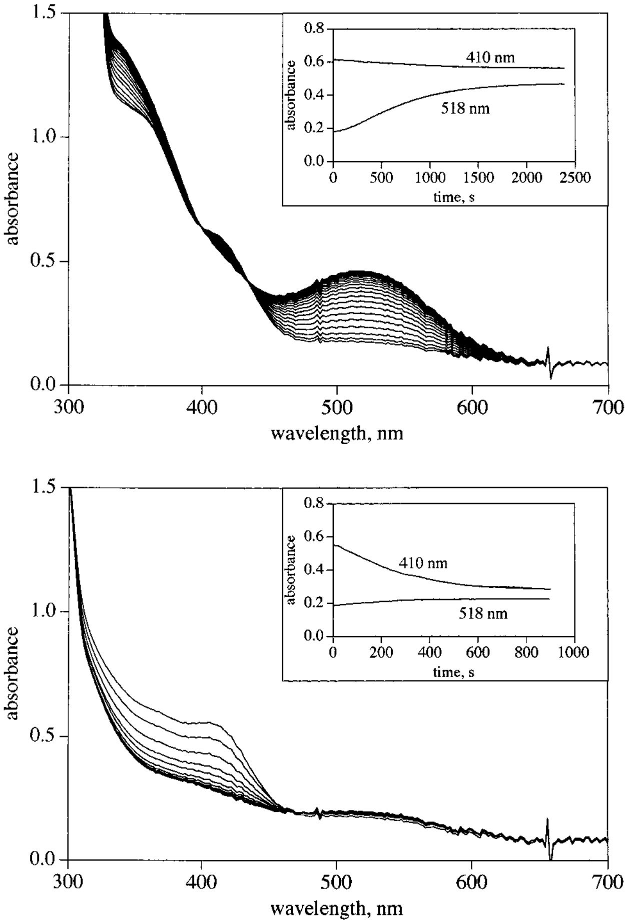

Figure 1. UV−vis spectral changes associated with the formation of the $Cr(CO)_4(dmbpy)$ chelate complex from $Cr(CO)_5(\mu\text{-dmbpy})Cr(CO)_5$ in toluene at 25 °C and $\Delta t = 100$ s: (a, top) [complex] = 1.2×10^{-4} M, [dmbpy] = 0.1 M (insert: absorbance vs time traces at two wavelengths); (b, bottom) [complex] = 1.1×10^{-4} M, no dmbpy added (insert: absorbance vs time traces at two wavelengths).

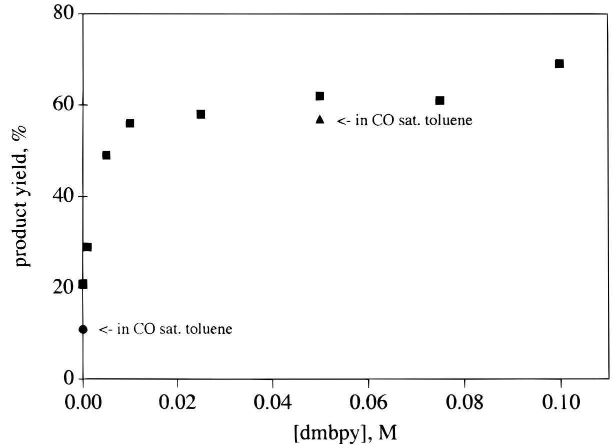

Figure 2. Yield of the $Cr(CO)_4(dmbpy)$ chelate complex based on the initial Cr content of $[Cr(CO)_5(\mu\text{-dmbpy})Cr(CO)_5]$. Calculations are based on ϵ for either $Cr(CO)_5(\mu\text{-dmbpy})Cr(CO)_5$ or $Cr(CO)_4dmbpy$. For experimental conditions, see Figure 3.

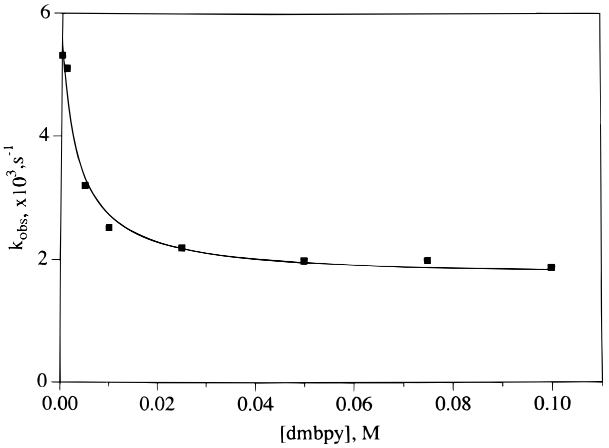

Figure 3. Rate constant k_{obs} for the chelate ring-closure step in the formation of $Cr(CO)_4(dmbpy)$ from $Cr(CO)_5(\mu\text{-dmbpy})Cr(CO)_5$ ($\sim 1.2 \times 10^{-4}$ M) monitored at $\lambda = 518$ nm in toluene at 25 °C as a function of added dmbpy under an inert atmosphere.

However, at high dmbpy concentration, the chelate complex is formed as the main product (Figure 2).[18] Kinetic traces recorded at 518 nm, where the appearance of $Cr(CO)_4(dmbpy)$ is observed, exhibit a two-step process under all conditions. Figure 1a shows a typical absorbance-time trace at 518 nm and high ligand concentration (0.1 M dmbpy), which clearly exhibits an induction period. This means that it takes some time to build up a reactive intermediate that subsequently undergoes ring-closure. Such a reaction scheme will consist of

$$A \rightleftharpoons B \rightarrow C$$

where A, B and C represent the dinuclear species, $Cr(CO)_5(dmbpy)$, and $Cr(CO)_4(dmbpy)$, respectively. The observed spectral changes were analyzed using Specfit global analysis,[26] which confirmed the formation of an intermediate species. The disappearance of $[Cr(CO)_5]_2(\mu\text{-dmbpy})$ monitored at 410 nm also exhibits a two-step process, especially at low dmbpy concentrations (Figure 1b). It was our primary aim to study the formation of $Cr(CO)_4(dmbpy)$, and we therefore followed the growth of the MLCT band at 518 nm in our kinetic measurements. For the conditions selected in this study it was always better to analyze the traces at the longer wavelength, since the change in absorbance at 410 nm, which is related to that of the bridged complex, becomes too small at high ligand concentration. A series of preliminary experiments indicated that the faster step is independent of the concentration of added dmbpy, whereas the slower step significantly decreased in rate with increasing ligand concentration. Due to the small changes in absorbance at 518 nm at low [dmbpy], the first (faster) exponential function could not be resolved clearly under all condititons and an average rate value of $(3.8 \pm 0.4) \times 10^{-3}$ s^{-1} was found at 25 °C. Due to the fact that this reaction is independent of the dmbpy concentration, we conclude that it must be associated with the dissociation of the dinuclear complex.

The values for the second exponential function, measured at 518 nm, decrease significantly with increasing dmbpy concentration (Figure 3) and reach a limiting value of $k_{obs} = 1.87 \times 10^{-3}$ s^{-1} at 25 °C and a dmbpy concentration of 0.1 M. This finding contradicts the reported behavior of this complex, for which an increase

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in k_{obs} with increasing dmbpy concentration was found.[18] We have no simple explanation for this apparent discrepancy other than that it may be related to the interference of the preceding faster step, which was not recognized in the previous study.[18]

We observe the same trends in the yield for the conversion into the ring-closed complex (Figure 2) as found by Long et al.[18] It was shown that in the presence of CO (saturated toluene 0.009 M)[27] the disappearance of the bridged complex was accelerated and the formation of the ring-closed product was suppressed due to the formation of $Cr(CO)_6$.[18] The rates for the disappearance of the ring-opened species under these conditions was found to be 14.1×10^{-3} and 6.8×10^{-3} s^{-1} at 410 nm, whereas nearly no formation of $Cr(CO)_4$(dmbpy) could be observed at 518 nm.

When both dmbpy (0.05 M) and CO (0.009 M) are present, we do observe the formation of the ring-closed product at 518 nm (see Figure S1 in the Supporting Information). The observed rates show that the presence of CO slows down the second step, formation of $Cr(CO)_4$(dmbpy), to a value of $k_{obs} = 8.8 \times 10^{-4}$ s^{-1}, whereas the first-exponential function seems not to be affected. Analysis of the UV−vis spectra resulted in a yield of more than 57% (see also Figure 2) based on the starting material.

At high [dmbpy], our k_{obs} value of 1.87×10^{-3} s^{-1} is in reasonable agreement with the reported limiting rate constant of 1.2×10^{-3} s^{-1} under similar conditions.[18] Thus, the limiting rate constant reached at high dmbpy concentration represents the situation where $Cr(CO)_4$(dmbpy) is produced from $Cr(CO)_5$(dmbpy) and possible side reactions are eliminated. A possible mechanism for the reaction was suggested by Long et al.[18]

Scheme 1

$$(Cr(CO)_5)_2(\mu\text{-dmbpy}) + S \rightleftharpoons Cr(CO)_5(\text{dmbpy}) + Cr(CO)_5S \quad (4)$$

$$Cr(CO)_5(\text{dmbpy}) + S \rightleftharpoons Cr(CO)_5(S) + \text{dmbpy} \quad (5)$$

$$Cr(CO)_5(\text{dmbpy}) \longrightarrow Cr(CO)_4(\text{dmbpy}) + CO \quad (6)$$

$$Cr(CO)_5S + CO \longrightarrow Cr(CO)_6 + S \quad (7)$$

According to Scheme 1, the bridged pentacarbonyl complex dissociates into $Cr(CO)_5$(dmbpy) and $Cr(CO)_5$(S), the former of which can either lose dmbpy in (5) or undergo ring closure in (6), whereas $Cr(CO)_5$(S) can either react with free dmbpy when available in (5), followed by chelation, or react with CO to produce $Cr(CO)_6$ in (7). It follows that the decay of the bridged complex will only result in a very low concentration of the ring-closed $Cr(CO)_4$(dmbpy) complex in the absence of or at low concentrations of added dmbpy due to the side reaction included in the scheme, which is responsible for the low yield of $Cr(CO)_4$(dmbpy). On the addition of sufficient dmbpy, dissociation of the dimer leads to the exclusive formation of $Cr(CO)_5$(dmbpy) and mainly conversion to $Cr(CO)_4$(dmbpy); i.e., added dmbpy favors the trapping of $Cr(CO)_5$(S) and suppresses the dissociation of $Cr(CO)_5$(dmbpy) according to (5) and so favors the chelation step (6).[18] The presence of two-exponential decays at 410 nm, as well as two-exponential growths at 518 nm, must be related to the two subsequent reactions outlined in Scheme 1: the first involving dissociation of the bridged complex and the second ring closure of the $Cr(CO)_5$(dmbpy) species.

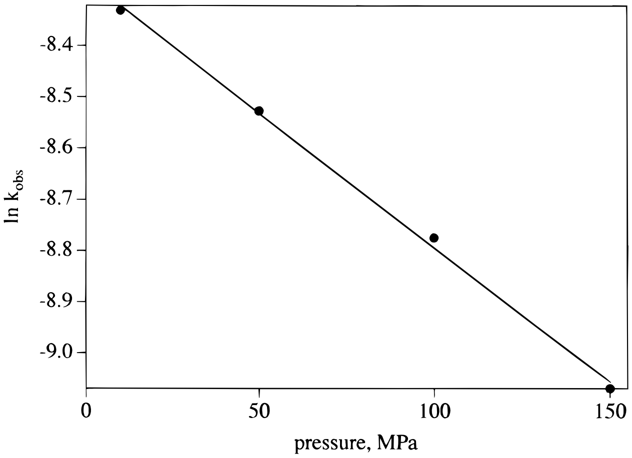

Figure 4. Pressure dependence of the ring-closure reaction of $Cr(CO)_5(\mu\text{-dmbpy})Cr(CO)_5$ ([complex] $\approx 1.2 \times 10^{-4}$M, [dmbpy] = 0.1 M, $T = 11.7$ °C.

Since the slower rate, k_{obs}, is suggested to be related to the ring-closure reaction, activation parameters were determined for this reaction step. The pressure dependence of the reaction was studied at 0.1 M dmbpy, i.e., where k_{obs} reaches a minimum in Figure 3, and the results are summarized in Figure 4. The yield of $Cr(CO)_4$(dmbpy) at elevated pressure was in the same range as for reactions at ambient pressure (ca. 70%). The volume of activation of $+12.5 \pm 0.4$ cm^3 mol^{-1} for the ring-closure reaction (6), evaluated from the slope in Figure 4, strongly supports the operation of a dissociative mechanism (see following discussion). The temperature dependence of this reaction was studied under similar conditions, and the associated activation parameters are summarized in Table 1. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are typical for dissociative reactions (see further discussion).

B. Irradiation of $Cr(CO)_6$ in the Presence of dmbpy. The isolation of the bridged complex and its transformation in solution to $Cr(CO)_4$(dmbpy) and $Cr(CO)_6$ raised the question of the possible role of this species during the chelation reaction of $Cr(CO)_5$(dmbpy) generated photochemically in solution from a mixture of $Cr(CO)_6$ and dmbpy. To compare the above-reported results with the thermal ring-closure reaction of $Cr(CO)_5$(dmbpy) generated photochemically, the latter reaction was also studied in detail as a function of [dmbpy]. Although we have no spectroscopic evidence for the formation of $Cr(CO)_5$(dmbpy) instead of $[Cr(CO)_5]_2(\mu\text{-dmbpy})$, it is obvious that the large excess of dmbpy (0.1 M dmbpy) used to study the temperature and pressure dependence of the reaction will favor the formation of the monomeric species in solution. Furthermore, is is also reasonable to consider the formation of $Cr(CO)_4(\text{dmbpy})_2$ during the period of irradiation, which will also lead to the ring-closed $Cr(CO)_4$(dmbpy) product. According to available literaure data,[28] complexes of the type *cis*-$Cr(CO)_4(\text{py-R})_2$ exhibit absorbance spectra rather similar to those of related ring-closed species. This would, however, mean that the expected spectral changes asociated with the ring closure of Cr-

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Table 1. Activation Parameters for the Thermal Ring-Closure Reaction[a]

complex	solvent	k_{obs},[b,d] s^{-1}	$\Delta V^{\ddagger}$,[b,d] $cm^3\ mol^{-1}$	$\Delta H^{\ddagger}$,[d] $kJ\ mol^{-1}$	$\Delta S^{\ddagger}$,[d] $J\ mol^{-1}\ K^{-1}$	ref
$Cr(CO)_5$−dab	*n*-heptane	2.7×10^{-5}		37 ± 2[f]	-204 ± 5[f]	19
$Cr(CO)_5$−dab	*n*-heptane	3.4×10^{-5}	$+14.3 \pm 1$	125 ± 9	93 ± 29	*e*
$Cr(CO)_6$ + dab + *hν*	toluene	1.52×10^{-4}	$+17.2 \pm 1$	81 ± 2	-47 ± 7	11
$[Cr(CO)_5]_2$(*μ*-dmbpy)	toluene	1.2×10^{-3}		110	51	18
$[Cr(CO)_5]_2$(*μ*-dmbpy)	toluene	1.87×10^{-3}	$+12.5 \pm 0.4$[c]	101 ± 4	42 ± 13	*e*
$Cr(CO)_6$ + dmbpy + *hν*	toluene	3.33×10^{-3}	$+17.9 \pm 0.8$[c]	81 ± 2	-22 ± 8	*e*

[a] Experimental conditions: [Cr] = (1−5) × 10^{-4} M. [b] At 25.0 °C. [c] At 11.7 °C. [d] Measured under limiting conditions, i.e., $k_{obs} = k_3$. [e] This work. [f] Recalculated from the data in ref 19.

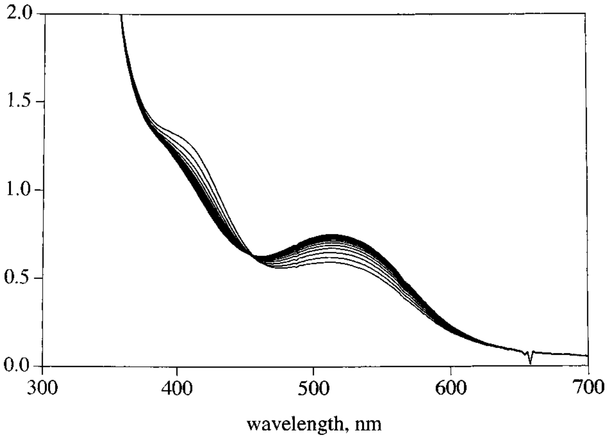


Figure 5. UV−vis spectral changes associated with the formation of the $Cr(CO)_4(dmbpy)$ chelate complex after 20 s irradiation of $Cr(CO)_6$ (5×10^{-4} M) in the presence of excess dmbpy (0.1 M) in toluene at 25 °C and $\Delta t = 100$ s.

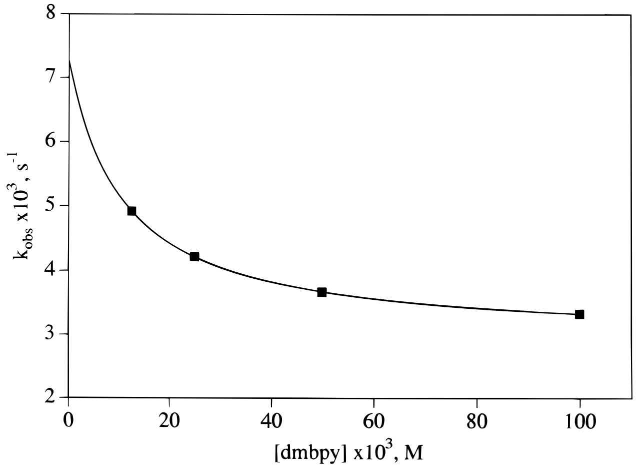


Figure 6. Concentration dependence of k_{obs} for the photoinduced ring-closure reaction of $Cr(CO)_6$ + dmbpy (T = 25 °C, [Cr] = 5×10^{-4} M).

$(CO)_4(dmbpy)_2$ will be significantly smaller than those associated with the ring closure of $Cr(CO)_5(dmbpy)$.

The observed spectral changes were similar to those reported in an earlier study[18] and in Figure 1, and a typical example is shown in Figure 5. The initial absorption at 518 nm must be due to the formation of either *cis*-$Cr(CO)_4(dmbpy)_2$ or the ring-closed product during the irradiation of the $Cr(CO)_6$/dmbpy solution. Absorbance time plots at 410 and 518 nm clearly indicate two exponential decays at the former and a two-exponential growth of the product at the latter wavelength, respectively. The slower rate constant related to the product formation (i.e. ring closure) also decreases significantly with increasing [dmbpy] (Figure 6) and reaches a limiting value of 3.18×10^{-3} s^{-1} at 0.1 M dmbpy, 518 nm, and 25 °C. The first step is ca. 10 times faster, but we were not able to obtain accurate values due to the dead time of the experimental method. The rapid decay, observed as the fast step at low [dmbpy] and 410 nm, can be related to the participation of different pentacarbonyl species in which solvent, dmbpy, and possible solvent impurities compete for the available coordination site. In addition, this reaction may also involve the formation of a dmbpy-bridged complex. The subsequent slow reaction, which represents the main contribution at high [dmbpy], is ascribed to the ring closure of $Cr(CO)_5(dmbpy)$ observed at 518 nm. The values of k_{obs} and the overall observed trends are similar to those observed for the reaction of the bridged complex reported in Figure 3. The possible participation of a bis-substituted species, $Cr(CO)_4(dmbpy)_2$, due to secondary photolysis of initially generated $Cr(CO)_5(dmbpy)$, was taken into account. The reactions shown in Scheme 2 are suggested to account for the reported behavior.

Scheme 2

$$Cr(CO)_6 + S \xrightarrow{h\nu} Cr(CO)_5S + CO \quad (8)$$

$$Cr(CO)_5S + dmbpy \overset{fast}{\rightleftharpoons} Cr(CO)_5(dmbpy) + S \quad (9)$$

$$Cr(CO)_5(dmbpy) + S \xrightarrow{h\nu} Cr(CO)_4(dmbpy)(S) + CO \quad (10)$$

$$Cr(CO)_4(dmbpy)(S) + dmbpy \overset{fast}{\rightleftharpoons} Cr(CO)_4(dmbpy)_2 + S \quad (11)$$

$$Cr(CO)_5(dmbpy) + Cr(CO)_5S \rightleftharpoons (Cr(CO)_5)_2(\mu\text{-dmbpy}) + S \quad (12)$$

$$Cr(CO)_5S + CO \longrightarrow Cr(CO)_6 + S \quad (13)$$

$$Cr(CO)_5(dmbpy) + S \rightleftharpoons Cr(CO)_4(dmbpy)(S) + CO \quad (14)$$

$$Cr(CO)_4(dmbpy)(S) \xrightarrow{fast} Cr(CO)_4(dmbpy) + S \quad (15)$$

Reactions 8 and 10 are the photoinduced reactions, whereas the others are the possible thermal reactions following the event of photolytic CO loss. Reaction 12 was included since the dinuclear complex was isolated as mentioned before.[18] We have no real evidence for its appearance in solution during the photoinduced reaction, but it seems obvious to us that we have to consider this possibility.

The temperature and pressure dependence of this reaction was studied at high [dmbpy] where reaction 14 is suggested to be the rate-determining step. The values of k_{obs} decrease significantly with increasing pressure (see Figure S2 in the Supporting Information) and the associated volume of activation, +17.9 ± 0.8 $cm^3\ mol^{-1}$, strongly supports the operation of a dissociative mechanism (see further discussion). The activation parameters are summarized along with others measured in this and related studies in Table 1. A ring-closure proccess starting from the more labile $Cr(CO)_4(dmbpy)_2$ is a possible explanation for the higher limiting rate and the lower $\Delta H^{\ddagger}$ value found for the photoiniti-

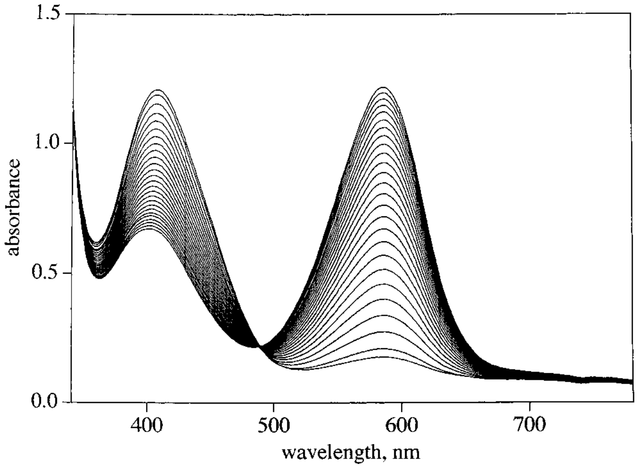


Figure 7. UV−vis spectral changes associated with the formation of the $Cr(CO)_4(dab)$ chelate complex from $Cr(CO)_5(dab)$ (0.9×10^{-4} M) in the presence of excess dab (80 mM) at a pressure of 150 MPa in *n*-hexane at 25 °C and $\Delta t = 30$ min.

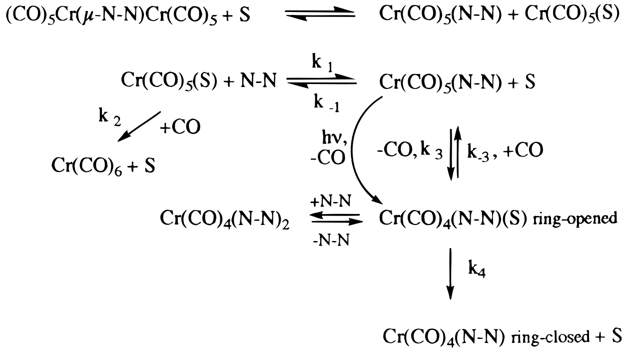
ated reaction compared to those starting with the isolated complexes (Table 1). Because a dmbpy ligand is larger than a CO, this would also explain the higher activation volume in the case of the photoinitiated reaction (Table 1) (see further discussion).

C. Thermal Behavior of $Cr(CO)_5$dab. The dab complex was isolated in its nonbridged form. The spectral changes observed for the ring-closure reaction in *n*-hexane at 150 MPa are in good agreement with those reported before at ambient pressure (see Figure 7).[19] The concentration dependence of the first-order kinetics, monitored at 586 nm, exhibits the same trend as reported above for the dmbpy system (see Figure S3 in the Supporting Information). A limiting rate constant of $k_{obs} = 3.4 \times 10^{-5}\ s^{-1}$ was found at 0.080 M dab and 25 °C, which is in close agreement with the value of $2.7 \times 10^{-5}\ s^{-1}$ reported for 23 °C and [dab] = 0.067 M.[20] The temperature and pressure dependence of the chelation reaction was studied under these conditions, and the observed volume of activation of $+14.3 \pm 1.0$ $cm^3\ mol^{-1}$ (see Figure S4 in the Supporting Information) is close to the value of $+17.2 \pm 1.0$ $cm^3\ mol^{-1}$ reported for the photoinduced reaction in the $Cr(CO)_6$/dab system.[11] The associated thermal activation parameters are summarized along with literature data in Table 1. The significantly more positive $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values found in the present study compared to those reported before[11,19] are ascribed to the selection of more appropriate reaction conditions, i.e., high chelate concentration, in the present study.

For this system we can suggest a reaction scheme similar to that for the bridged dmbpy complex, with the only difference being that the mononuclear species is the starting material. The ring-closure reaction will compete with the formation of $Cr(CO)_6$, which will in turn depend on the selected concentration of free dab. At high [dab], chelation will be rate-determining and represent the limiting rate constant under such conditions.

D. Overall Comparison and Suggested Mechanism. Very similar kinetic trends were observed for all the systems studied in this investigation. Independent of whether the reaction is initiated thermally from the isolated $\{Cr(CO)_5\}_2(\mu\text{-dmbpy})$ or $Cr(CO)_5(dab)$ complexes or photochemically from $Cr(CO)_6$/bidentate ligand mixtures, the observed rate constants decrease significantly on increasing the chelating ligand concentration (compare Figures 3, 6, and S3). The limiting rate constant clearly represents the ring-closure reaction of the $Cr(CO)_5(N{-}N)$ species in all cases. A general mechanism that can account for all the observations is presented in Scheme 3. The nature of the starting material in solution will depend on the position of the first equilibrium between the bridged and the mononuclear complexes, $\{Cr(CO)_5\}_2(\mu\text{-}N{-}N)$ and $Cr(CO)_5(N{-}N)$, where N−N = dmbpy or dab. The $Cr(CO)_5(S)$ species (S = solvent), produced via thermal dissociation of the dinuclear complex or photoinduced CO dissociation from $Cr(CO)_6$, will in the presence of an excess of N−N be almost fully converted to $Cr(CO)_5(N{-}N)$, followed by rate-determining chelation to $Cr(CO)_4(N{-}N)$.

Scheme 3



The equilibrium between the dinuclear complex and the two $Cr(CO)_5$ species in Scheme 3 exists in solution and can account for the isolation of $(CO)_5Cr(\mu\text{-}N{-}N)Cr(CO)_5$ in the dmbpy case. Moreover, the ^1H and ^{13}C NMR spectra of isolated $(CO)_5Cr{-}N{-}N$ (N−N = dab) exhibit evidence for the formation of $(CO)_5Cr(\mu\text{-}N{-}N)Cr(CO)_5$ in solution.[20] We consider the formation of the bridged species to be a dead end with respect to the ring-closure process. We exclude a direct formation of the chelated $Cr(CO)_4(N{-}N)$ from the bridged compound because of the induction period as shown in Figure 1a. All evidence we have at present indicates that the mononuclear $(CO)_5Cr(N{-}N)$ species is the actual one that undergoes ring closure. The formation of $(CO)_5Cr(S)$ and $(CO)_5Cr(\mu\text{-}N{-}N)Cr(CO)_5$ should be considered as side reactions that do not contribute to the formation of the ring-closed $(CO)_4Cr(N{-}N)$ product. For all practical purposes the ring-closure kinetics is controlled by the second part of Scheme 3, since the first part is related to the rapid dissociation of the dimeric species. We assume, on the basis of the activation parameters, that the chelate complex formation involves dissociative loss of a carbonyl ligand to produce a $Cr(CO)_4(N{-}N)(S)$ ring-opened species which can undergo rapid ring closure. The formation of such solvento species has been suggested in the literature to result from the highly cis-labilizing influence of the N-donor ligand.[29,30] The suggestion is supported by the observed behavior when both potential ligands, dmbpy and CO, are available in large excess. The rate for the formation of the ring-

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[30] Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 1679.

Table 2. Calculated Rate Constants for the Ring-Closure Reaction of Pentacarbonyl Complexes According to Scheme 3 and Eq 17[a]

complex	$k_{-1}k_2$[CO], s^{-2}	k_2[CO], s^{-1}	k_{-1},[c] s^{-1}	k_1, M^{-1} s^{-1}	k_3, s^{-1}
$(CO)_5Cr(\mu\text{-dmbpy})Cr(CO)_5$	3.7×10^{-3}	0.97	3.8×10^{-3}	260	1.7×10^{-3}
$Cr(CO)_6 + h\nu +$ dmbpy	1.0×10^{-2}	2.29	4.4×10^{-3}	212	2.9×10^{-3}
$Cr(CO)_5$-dab[b]	9.8×10^{-5}	1.12	8.7×10^{-5}	562	2.3×10^{-5}

[a] At 25 °C. [b] At 23 °C. [c] Calculated from k_1k_2[CO]/k_2[CO].

closed product is then decelerated to $k_{obs} = 8.8 \times 10^{-4}$ s^{-1}, whereas the yield of the ring-closed species is high (see Figure 2).

When the decay of $Cr(CO)_5$(N−N), or of $(CO)_5Cr(\mu$-dmbpy)$Cr(CO)_5$ via $Cr(CO)_5$(N−N), with formation of $(CO)_4$Cr(N−N) is monitored, k_{obs} decreases with increasing [N−N]. The rate law for the suggested mechanism accounts for this observation. Application of the steady-state approximation to $Cr(CO)_5$(S) and ring-opened $Cr(CO)_4$(N−N)(S) in Scheme 3 results in eq 16.

$$k_{obs} = \frac{k_{-1}k_2[\mathrm{CO}]}{k_1[\mathrm{N{-}N}] + k_2[\mathrm{CO}]} + \frac{k_3k_4}{k_{-3}[\mathrm{CO}] + k_4} \quad (16)$$

The higher value of k_{obs} at low [N−N] is due to an additional reaction path in which $Cr(CO)_5$(N−N) decomposes to $Cr(CO)_6$ via the solvento species. This decomposition is suppressed at higher [N−N], such that only the slow ring-closure reaction is observed under such conditions. There are related reports in the literature in which the authors also observed a decrease in the rate constant with increasing nucleophile concentration.[31−33] It was therefore assumed that parallel reaction pathways, involving the solvent, account for this unexpected behavior.

The experimental data in Figures 3, 6, and S3 for the chelation of $Cr(CO)_5$(dmbpy) and $Cr(CO)_5$(dab), respectively, in the absence of added CO were fitted by a nonlinear least-squares analysis to an approximate expression (eq 17) for eq 16 under the assumption that

$$k_{obs} = \frac{k_{-1}k_2[\mathrm{CO}]}{k_1[\mathrm{N{-}N}] + k_2[\mathrm{CO}]} + k_3 \quad (17)$$

k_{-3}[CO] ≪ k_4; i.e., ring closure is rapid compared to recoordination of CO. The fits are presented as solid lines in the figures, and the values for the fitted rate constants are listed in Table 2. The k_3 data calculated in this way are in good agreement with the experimental k_{obs} values found at high [N−N] for the ring-closure reaction. The almost constant value for k_2[CO] is such that it is usually significantly smaller than k_1[N−N], which accounts for the effective formation of the chelated complex, even in the presence of CO at high ligand concentrations. The approximate rate law (17) does not, of course, account for the lower k_{obs} values observed for the ring-closure reaction in CO-saturated solution containing dmbpy in high concentration, since this behavior can only be rationalized on the basis of the second term in eq 16. The values of k_1 are in agreement with the higher nucleophilicity of the dab ligand as compared to dmbpy.

The significantly higher value of k_3 for chelation of $Cr(CO)_5$(dmbpy) as compared to k_3 for chelation of $Cr(CO)_5$(dab) is rather surprising, because of the lower basicity of dmbpy ($pK_b = 9.1$) as compared to dab ($pK_b = 3.3$).[34,35] The generally slower rates for dab ring closure can be explained in terms of steric interaction of the β-hydrogen in the mononuclear intermediate complex. The relatively large steric interaction of the CH group close to the metal center and the carbonyl will support the rotation around the central C−C bond in the case of the bpy type complexes, in contrast to the less confined position in the dab complex.[8] Similar arguments were used to account for the very different chelation rate constants found for ethylenediamine, dab, bipyridine, and phenanthroline.[9,11]

The thermal and pressure activation parameters for the investigated chelation reactions are summarized in Table 1. The significantly different k_{obs} values reported for the ring closure of $(CO)_5$Cr(dab) must be partially due to the different solvents employed, *n*-heptane in the thermal vs toluene in the photoinduced process. The solvent will largely affect the ring-closure rate through the solvation of the dangling N-donor and the dissociating CO. The thermal and photoinduced ring-closure reactions exhibit very similar activation volumes under limiting ligand concentration conditions, and the results are such that they strongly support the operation of a limiting dissociative (D) mechanism. Other examples in the literature in which CO is displaced in a dissociative way have revealed volumes of activation of between +14 and +24 cm^3 mol^{-1}. For example, the dissociative substitution of CO in $Cr(CO)_4$(phen) by $P(OMe)_3$ as entering nucleophile was characterized by a large volume of activation of $+13.8 \pm 0.5$ $cm^3 mol^{-1}$.[36] For the dissociation of CO from $[Ru_3(CO)_{11/10}]^-$ cluster compounds, activation volumes from +16 to +24 cm^3 mol^{-1} were reported.[37]

The thermal activation parameters listed in Table 1 differ significantly, depending on the experimental conditions selected for the measurements (see earlier discussion). In a few cases the chelation reactions exhibit $\Delta H^\ddagger$ values of more than 100 kJ mol^{-1} and significantly positive $\Delta S^\ddagger$ values, which are typical for dissociation of CO prior to ring closure.[38] The larger values for the activation enthalpy and entropy as well as the lower activation volume in the case of the thermal ring closure of the isolated $Cr(CO)_5$(N−N) complexes, compared to the lower values of the thermal activation parameters and the higher volume of activation for the photoinitiated reaction, can possibly be accounted for

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in terms of the formation of $Cr(CO)_4(N-N)_2$ at high ligand concentration. This species will also form the ring-closed $Cr(CO)_4(N-N)$ complex according to a dissociative mechanism path, but as seen from the activation parameters, the leaving group (N−N) is significantly larger ($+17 > 12-14$ cm^3 mol^{-1}, $\Delta V^{\ddagger}$) and were weakly bound to the Cr center ($81 < 101-125$ kJ mol^{-1}, $\Delta H^{\ddagger}$) than CO in $Cr(CO)_5(N-N)$. This could also explain the higher limiting k_{obs} in the case of $Cr(CO)_6$ + dmbpy + $h\nu$ as compared to the value for the isolated compound $(CO)_5Cr(\mu\text{-dmbpy})Cr(CO)_5$.

We conclude that the results of this study have contributed to resolving some apparent discrepancies in the literature and have revealed the intimate nature of the ring-closure reaction of pentacarbonylchromium complexes in more detail. The competition with side reactions, such as formation of bridged and bis-substituted compounds, solvento species, and recombination with CO to produce the hexacarbonyl complex, complicates the treatment and understanding of "simple" chelation kinetics. However, when a sufficiently high concentration of the chelating ligand is selected, then clean ring-closure kinetics are obtained and all side reactions can be largely suppressed. Important to note is our definitive finding that these "simple" ring-closure reactions do not follow the expected associative displacement of CO but, rather, involve a prior rate-determining dissociation of CO (displacement by solvent) followed by a rapid ring-closure step.

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Supporting Information Available: Tables of k_{obs} values as a function of concentration, temperature, and pressure and figures giving spectra and data plots (Figures S1−S4) (8 pages). Ordering information is given on any current masthead page.

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