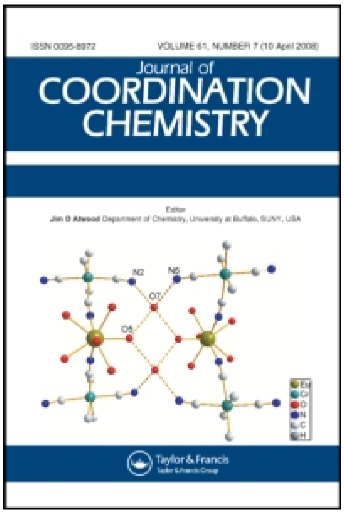

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

RATES OF RING-OPENING OF 2,2,4,7,7-PENTAMETHYL-3,6-DITHIAOCTANE TETRACARBONYL TUNGSTEN (0)

José E. Cortés-Figueroa[a]; Jesús A. Rodríguez[a]
[a] Organometallic Chemistry Research Laboratory, Department of Chemistry, University of Puerto Rico, Mayagüez, PR

To cite this Article Cortés-Figueroa, José E. and Rodríguez, Jesús A.(1998) 'RATES OF RING-OPENING OF 2,2,4,7,7-PENTAMETHYL-3,6-DITHIAOCTANE TETRACARBONYL TUNGSTEN (0)', Journal of Coordination Chemistry, 44: 1, 141 — 150

To link to this Article: DOI: 10.1080/00958979808022888

URL: http://dx.doi.org/10.1080/00958979808022888

J. Coord. Chem., 1998, Vol. 44, pp. 141–150
Reprints available directly from the publisher
Photocopying permitted by license only

RATES OF RING-OPENING OF 2,2,4,7,7-PENTAMETHYL-3,6-DITHIAOCTANE TETRACARBONYL TUNGSTEN (0)[†]

JOSÉ E. CORTÉS-FIGUEROA* and JESÚS A. RODRÍGUEZ[1]

[a]*Organometallic Chemistry Research Laboratory, Department of Chemistry, University of Puerto Rico, Mayagüez PR 00681*

(Received 20 February 1997; Revised 13 May 1997; In final form 22 September 1997)

Ring displacement from η^2-PDOW(CO)$_4$ (PDO = 2,2,4,7,7-pentamethyl-3,6-dithiaoctane) by L (L = P(O-i-Pr)$_3$ and P(OEt)$_3$) produces a mixture of *cis*- and *trans*- (L)$_2$W(CO)$_4$. Results from kinetics experiments are consistent with the results observed for the structurally-related η^2-DTOW(CO)$_4$ complex (DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane). A smaller value for the rate constant (k_1) for the ring-opening step of η^2-PDOW(CO)$_4$ reflects the shorter W-S bond distances observed in η^2-PDOW(CO)$_4$. This observation is consistent with the trend observed for a series of η^2-DTAW(CO)$_4$ complexes (DTA = Dithiaalkanes) in which the value of k_1 increases with the size of the chelate ring. Since the species η^2-PDOW(CO)$_4$ and η^2-DTOW(CO)$_4$ are five-membered chelate complexes, differences in their molecular and kinetic parameters are being ascribed to the methyl group in the chelate backbone of η^2-PDOW(CO)$_4$. Our observations confirm earlier findings that small differences in the structure of DTA greatly affect the rates of ring-opening in η^2-DTAW(CO)$_4$ complexes.

Keywords: carbonyl complexes; mechanism; structure; ligand substitution

INTRODUCTION

The reactions of η^2-(dithiaalkane)W(CO)$_4$ complexes (dithiaalkane (DTA) = (CH$_3$)$_3$CS(CH$_2$)$_n$SC(CH$_3$)$_3$) which contain four, five, six, seven, and eight-membered chelate rings, with phosphites (L) exhibit a reaction stoichiometry as given by

$$\eta^2\text{-DTAW(CO)}_4 + 2L \rightarrow cis\text{- and } trans\text{-(L)}_2\text{W(CO)}_4 + \text{DTA} \qquad (1)^{2\text{-}6}$$

---

*Corresponding author. Fax: 809 265-3849

[†] In memory of Professor Mariel M. Muir, former professor of the University of Puerto Rico, Rio Piedras Campus.

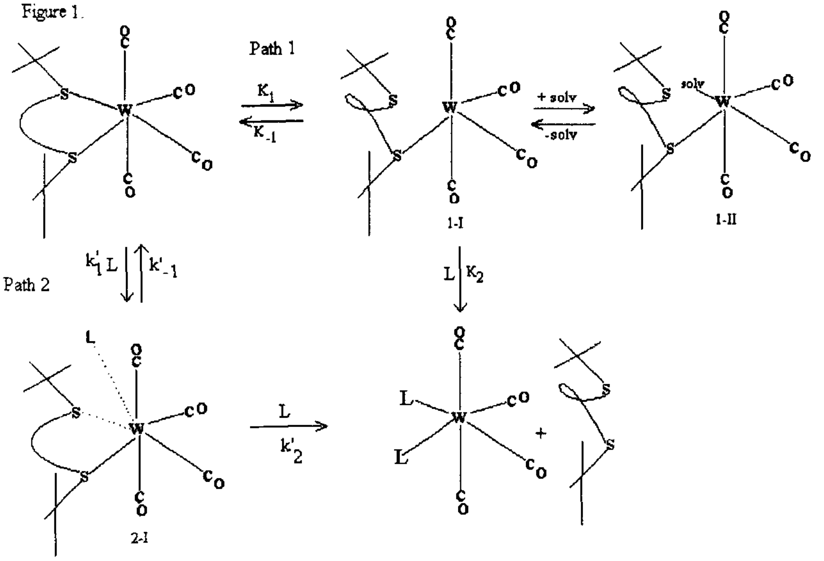

FIGURE 1 Proposed mechanism.

These reactions show a dependence on the size of DTA. For example, the reactions where n = 1, 4, and 5 for DTA = DTHp,[2] DTD,[3] and DTU,[3] respectively, proceed *via* a stepwise displacement according to

$$\eta^2\text{-DTAW(CO)}_4 + \text{L} \xrightarrow{k_{obsd}} cis\text{-}\eta^1\text{-DTA(L)W(CO)}_4$$

$$cis\text{-}\eta^1\text{-DTA(L)W(CO)}_4 + \text{L} \xrightarrow{k'_{obsd}} cis\text{- and } trans\text{-(L)}_2\text{W(CO)}_4 + \text{DTA} \qquad (2)$$

In these reactions the values $k_{obsd} \approx k'_{obsd}$ and the intermediates *cis*-η^1-DTA(L)W(CO)$_4$ are isolated and characterized. In the reactions of the five and six-membered rings (n = 2, 3; DTA = DTO,[4,5] DTN,[7] respectively) the stepwise displacement was not observed and it was proposed that the values $k_{obsd} \gg k'_{obsd}$ and that *cis*-η^1-DTA(L)W(CO)$_4$ are intermediate species at steady-state concentrations.

The rate-law for the first step, governed by k_{obsd} was interpreted in terms of the mechanisms described in Figure 1 (path 1). A large increase (7500-fold) in the value of the rate constant for ring-opening (k_1) was observed as the size of the chelate ring increases from five to eight atoms.[3] Interestingly, for η^2-

$DTHpW(CO)_4$ (four-membered ring) the observed rate-law was interpreted as a concerted ring-opening and reclosure (path 2 in Figure 1).[2]

Results from structural studies of (2,2,8,8-tetramethyl-3,7-dithianonane) tetracarbonyl tungsten(0) (six-membered ring, η^2-$DTNW(CO)_4$) and (2,2,7,7-tetramethyl-3,6-dithiaoctane) tetracarbonyl tungsten(0) (five-membered ring, η^2-$DTOW(CO)_4$) combined with the kinetics and mechanistic studies of their ligand exchange reactions have shown that small differences in the structural parameters of the chelate ring may affect the rates of ring-opening.[8] Further, results from x-ray crystallography of the complex η^2-$PDOW(CO)_4$ (five-membered ring, PDO = 2, 2, 4, 7, 7-pentamethyl-3,6-dithiaoctane) have shown that the major structural difference between η^2-$PDOW(CO)_4$ and the other two complexes is the observed *trans* influence and significantly shorter W-S bond lengths in the former complex.[9]

To further define the relationship between the structural parameters of the chelate ring and the rates and mechanisms of DTA displacement from η^2-$DTAW(CO)_4$ complexes, we have undertaken kinetics studies of the displacement of PDO from η^2-$PDOW(CO)_4$.

EXPERIMENTAL

General

Infrared spectra were obtained from a Nicolet 6000 Series 80 Fourier Transform spectrophotometer, NMR spectra from a Bruker 360 MHz spectrometer, and the visible spectra on a Perkin-Elmer UV Lambda 4B spectrophotometer. A Haake model FK circulator and a K/J Fluke digital thermometer equipped with a bead thermocouple were employed as temperature control devices. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Preparation and Purification of Materials

Xylenes (Adrich) were refluxed under argon over sodium for 24 h followed by fractional distillation. The ligands (L) (Aldrich), $P(O\text{-}i\text{-}Pr)_3$ and $P(OEt)_3$ were distilled under argon over sodium under reduced pressure (b 40°C/0.5 torr, $P(O\text{-}i\text{-}Pr)_3$; b 63°C/11 torr, $P(OEt)_3$).

PDO was prepared following a method described by Dobson and others.[2,3] One mole (23 g) of sodium was allowed to react with 500 mL of absolute ethanol in one liter three-necked flask equipped with a magnetic stirrer bar, reflux condenser, dropping funnel, and argon inlet. After all the sodium reacted, one mole (90 g) of t-butyl mercaptan (Aldrich) was added dropwise. Then, the reaction mixture was stirred for two h at room temperature. Under ice-cooling, 0.5 mole (109 g) of 1,2-dibromopropane (Baker) was added dropwise. The mixture was stirred for 10 h at room temperature followed by filtration under vacuum to remove the precipitated sodium bromide. The excess ethyl alcohol was removed by distillation and the reaction product was vacuum-distilled (82-84°C/2 torr) to yield 66 g of a colorless liquid. Anal. Calcd. for $C_{11}H_{24}S_2$(%): C, 59.99; H, 10.99; S, 29.08. Found: C, 59.85; H, 10.95; S, 29.08. ^{1}H NMR ($CDCl_3$) δ2.867 (m), 2.593 (m), 1.384 (d), 1.357 (s), 1.1.329 (s). ^{13}C NMR ($CDCl_3$) δ 37.877, 37.665, 31.570, 31.019, 23.148.

The η^2-PDOW(CO)$_4$ complex was prepared following the method reported for preparation of other η^2-DTAW(CO)$_4$ complexes.[5,6] In a 250-mL round-bottom flask equipped with a magnetic stirr bar and argon inlet, 0.0145 mole (5.10 g) of tungsten hexacarbonyl (Aldrich) was dissolved in 75 mL of xylenes and allowed to react with 0.0173 mole (3.820 g) of PDO. The reaction mixture was stirred and refluxed for 3.6 h. The resulting black solution was cooled to room temperature and suction filtered through a "cake" of celite under a continuous stream of argon. A bright-yellow solution was obtained and placed in the refrigerator. After 24 h a yellow powder was collected by suction filtration, washed with hot hexane (*ca.* 50 mL) and recrystallized from toluene/hexane. Bright-yellow crystals were obtained. The yield was 60%. Anal. Calcd. for $C_{15}H_{24}S_2O_4W$(%): C, 34.91; H, 4.69; S, 12.42. Found: C, 34.81; H, 4.68; S, 12.34. The carbonyl stretching spectrum in CH_2Cl_2 solution: 2017(w), 1896(s, sh), 1888 (s, sh), 1855 (m). ^{1}NMR ($CDCl_3$) δ 3.29 (m), 2.75 (m), 1.46 (s), 1.41 (s), 1.40(d). ^{13}C NMR ($CDCl_3$) δ 208.56, 207.24, 204.72, 50.36, 49.12, 42.82, 40.45, 29.54, 29.34, 21.48.

Kinetics Experiments

Kinetics experiments of the reactions of η^2-PDOW(CO)$_4$ with L were carried out under argon. The progress of the reactions was followed by monitoring the absorbance at 425 nm using a Perkin-Elmer UV Lambda 4B spectrophotometer. The reactions were studied under flooding conditions where [L]» [η^2-PDOW(CO)$_4$] so that [L] remained essentially constant.

Data Analysis

Data of the kinetics experiments were analyzed using a linear least-squares computer program developed for our personal computer. Error limits, given in parentheses as the uncertainties of the last digit(s) of the cited value, are one standard deviation.

TABLE I Values of k_{obsd} for reactions of η^2-PDOW(CO)$_4$ with L in xylenes.

Temperature (°C)	*L*	*[L], M*	$10^4k_{obsd}(s^{-1})$
71.3	P(O-i-Pr)$_3$	0.1972	0.0635(6)
		0.5149	0.1548(8)
		0.8274	0.2253(4)
		1.029	0.2734(4)
		1.222	0.3122(10)
		1.496	0.362(2)
		1.586	0.392(1)
81.3	P(O-i-Pr)$_3$	0.1612	0.156(8)
		0.4816	0.437(3)
		0.6124	0.539(2)
		0.7148	0.610(3)
		1.016	0.798(3)
		1.214	0.936(4)
		1.481	1.128(6)
		1.617	1.189(3)
91.3	P(O-i-Pr)$_3$	.2532	0.680(9)
		0.7997	1.91(2)
		0.8026	1.97(2)
		1.001	2.31(1)
		1.209	2.55(2)
		1.224	2.726(8)
		1.453	3.28(1)
		1.604	3.38(2)
91.3	P(OEt)$_3$	0.4503	2.03(6)
		0.6468	2.76(2)
		1.019	3.87(2)
		1.275	4.37(3)
		1.537	5.07(2)
		1.844	5.64(3)
		2.009	5.91(2)

RESULTS AND DISCUSSION

Plots of ln (A_t-A_{bl}) *vs* time are linear to at least two half lives (A_t = absorbance at time t; A_{bl} = absorbance of the blank since the reaction product does not significantly absorb at 425 nm). Given in Table I are the *pseudo*-first order rate constants (k_{obsd}) determined from the slopes of these plots. These rate constants show a strong dependence on [L]. Figure 2 and Figure 3 show that plots of k_{obsd} *vs* [L] are curved and that the reciprocal plots *i.e.*, 1/k_{obsd} *vs.* 1/[L] are linear. The reciprocal plots for L = P(O-i-Pr)$_3$ and P(OEt)$_3$ have different slopes but a common intercept. This kinetics behavior is expected on the basis of the proposed mechanism for closely-related systems.[2-5] For these systems the limiting mechanism, path 1 in Figure 1, was proposed. This mechanism involves an initial W-S bond breakage to form the electronically-unsaturated intermediate I-1 and the solvalted-intermediate I-2. The concentration of these intermediates are expected to be steady-state. Since the reactions were studied under flooding

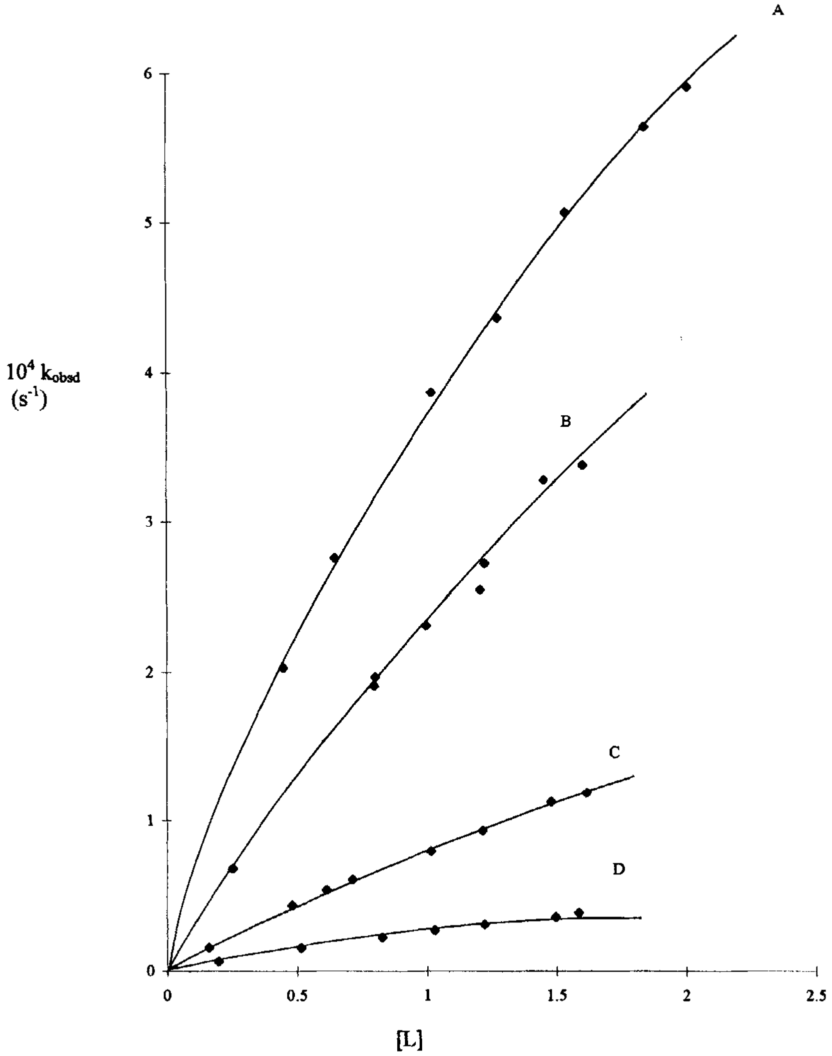

FIGURE 2 Plot k_{obsd} *vs.* [L] for the reactions of η^2-PDOW(CO)$_4$ with L in xylenes at three temperatures. A, at 91.3°, L = P(OEt)$_3$; B at 91.3°, L = P(O-i-Pr)$_3$; C, at 81.3°, L = P(O-i-Pr)$_3$; D, at 71.3°, L = P(O-i-Pr)$_3$.

conditions ($[L] \gg [\eta^2\text{-PDOW(CO)}_4]$), this mechanism predicts that the *pseudo*-first order rate constant is give by $k_{obsd} = k_1k_2[L]/k_{-1} + k_2[L])$. This equation predicts curved plots of k_{obsd} *vs.* [L] and linear plots of $1/k_{obsd}$ *vs.* $1/[L]$, since $1/k_{obsd} = ((k_{-1}/k_1k_2)1/[L]) + (1/k_1)$. Since k_1 is independent of L, plots for different L should have common intercepts. The value of k_1, calculated from the intercept, is the rate constant for ring-opening. The observed value of k_1 for L = $P(O\text{-}i\text{-}Pr)_3$ and $P(OEt)_3$ at 91.3°C, 12.7(10) $\times 10^{-4}$ and 13.0(4) $\times 10^{-4}$ s^{-1},

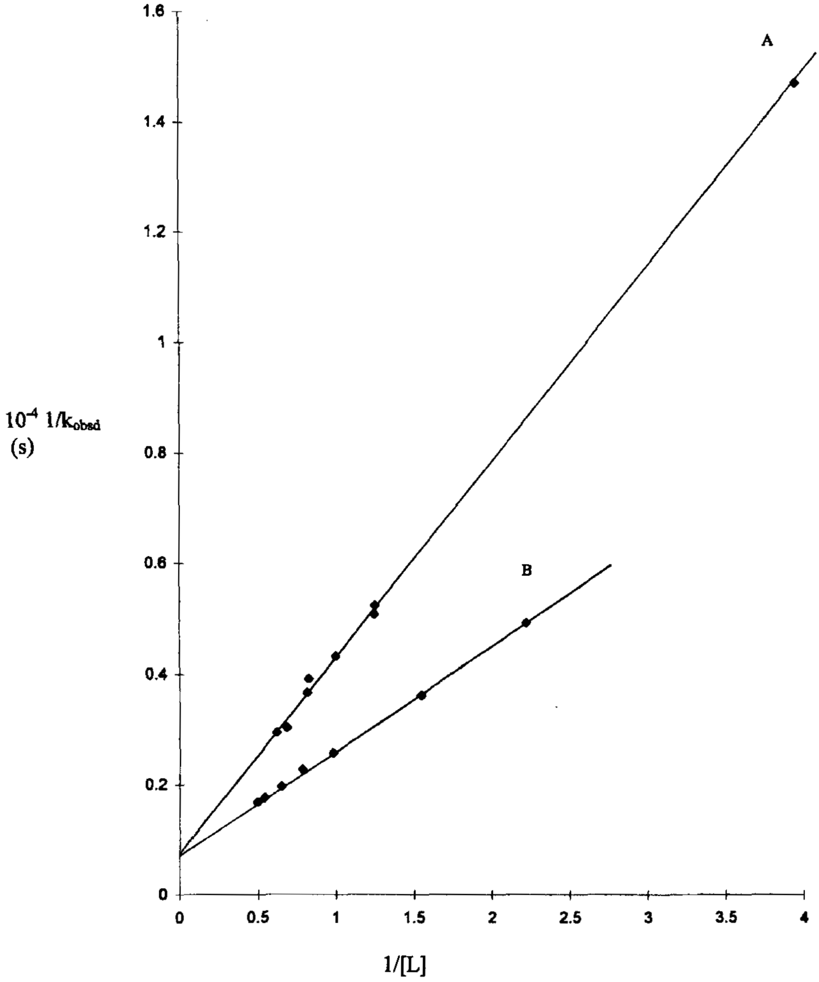

FIGURE 3 Plot $1/k_{obsd}$ *vs.* $1/[L]$ for the reactions of η^2-PDOW(CO)$_4$ with L = $P(O\text{-}i\text{-}Pr)_3$, $P(OEt)_3$ in xylenes at three temperatures. A at 91.3°, L = $P(OEt)_3$; B at 91.3°, L = $P(O\text{-}i\text{-}Pr)_3$.

TABLE II Rate constants and activation parameters for chelate ring-opening in η^2-PDOW(CO)$_4$.

Temperature (°C)	*L*	*10^4k_1 (s^{-1})*	*k_2/k_{-1} (M^{-1})*
71.3	P(O-i-Pr)$_3$	1.29(5)	0.26(1)
81.3		4.20(20)	0.24(2)
91.3		12.7(10)	0.22(2)
91.3	P(OEt)$_3$	13.0(4)	0.41(1)

$\Delta H_1^{\ddagger}$ = 28.0(2) kcal/mol

$\Delta S_1^{\ddagger}$ = 5.5(6) cal/deg-mol

$\Delta H_2^{\ddagger} - \Delta H_{-1}^{\ddagger} = -2.8(1)$ kcal/mol

TABLE III Structural and kinetics parameters of η^2-DTAW(CO)$_4$ complexes.

η^2-DTAW(CO)$_4$	10^5k_1 (s^{-1}) at 35.2°C	$\Delta H_1^{\ddagger}$ (Kcal/mol)	$\Delta S_1^{\ddagger}$ (cal/deg. mol)	W-S (Å)
DTA = PDO = $(CH_3)_3$ CS$((CH_3CH)(CH_2))$SC$(CH_3)_3$	0.08*	27.8(2)	5.5(6)	2.545(3)[a] 2.545(4)
DTA = DTO = $(CH_3)_3$ CS$(CH_2)_2$SC$(CH_3)_3$	0.16(3)	29.0(12)	1.8(37)	2.565(4)[b] 2.559(4)
DTA = DTN = $(CH_3)_3$ CS$(CH_2)_3$SC$(CH_3)_3$	6.5(5)	25.5(3)	− 5.2(8)	2.582(5)[b] 2.574(5)
DTA = DTD[c] $(CH_3)_3$ CS$(CH_2)_4$SC$(CH_3)_3$	810(3)	26.0(7)	18.0(23)	—
DTA = DTU[c] $(CH_3)_3$ CS$(CH_2)_5$SC$(CH_3)_3$	1210(50)	24.9(7)	14.7(23)	—

*Value estimated from the Eyring plot.

[a]reference 9, [b]reference 8, [c]reference 2

respectively, are consistent with this expectation. The competition ratios (k_2/k_{-1}), also given in Table II, suggest that the electronically-unsaturated intermediate η^1-PDOW(CO)$_4$ is slightly more selective toward the ring-closure step governed by k_1. The small decrease of the values of the ratios with increasing temperature suggest a higher enthalpy of activation for the ring-closure step ($\Delta H_{-1}^{\ddagger} > \Delta H_2^{\ddagger}$). It is instructive to compare the values of k_1 at 35.2°C given in Table III, for η^2-DTAW(CO)$_4$ complexes having chelate rings ranging from five to eight atoms. As the ring size increases from five to six atoms, the value of k_1 increases 40-fold a further 124-fold increase is observed when the ring size increases from six to seven atoms. Although, the trend of increasing value in k_1 with increasing ring size is observed when the ring size increases from seven to eight atoms, the observed increase is small (1.5-fold). Upon comparison of the value of k_1 for the two complexes having a five-membered ring, namely η^2-DTOW(CO)$_4$ and η^2-PDOW(CO)$_4$, one notices a small but significant increase (*ca.* 2-fold) in the value of k_1 for η^2-PDOW(CO)$_4$ relative to η^2-DTOW(CO)$_4$. The values of the W-S bond distances, given in Table III, mirror the observed trend for the values of k_1.

Comparison of the activation parameters (Table III) shows that the enthalpy of activation for the ring-opening ($\Delta H_1^{\ddagger}$) decreases with ring size. The entropy of activation ($\Delta S_1^{\ddagger}$) is expected to increase as the size of the chelate ring increases.[10] The complexes η^2-PDOW(CO)$_4$ and η^2-DTOW(CO)$_4$ have a chelate ring of the same size. The higher $\Delta S_1^{\ddagger}$ observed for η^2-PDOW(CO)$_4$ can be attributed to more distortion in the PDO chelate backbone during W-S bond breaking. This distortion is not, however, observed in the solid structure.[11]

CONCLUSIONS

A smaller value for the rate constant (k_1) for the ring-opening step of η^2-PDOW(CO)$_4$ among the series of η^2-DTAW(CO)$_4$ complexes reflects the shorter W-S bond distances observed for η^2-PDOW(CO)$_4$. This observation is consistent with earlier findings that small differences in the structure of the complexes greatly affect the rates of ring-opening.

Acknowledgments

This research was financially supported by the National Science Foundation (NSF-HRD 9550705) and the Puerto Rico Alliance for Minority Participation (NSF PR-AMP). The authors are very grateful for the NMR measurements provided by Professor David F. Wiemer from The University of Iowa.

References

1. Participant of the Undergraduate Research Program of the University of Puerto Rico.
2. G.R. Dobson, and J.E. Cortés, *Inorg. Chem.* **27**, 3308 (1988).
3. G.R. Dobson, and J.E. Cortés, *Inorg. Chem.* **28**, 539 (1989).
4. G.R. Dobson, C.B. Dobson, and S.E. Mansour, *Inorg. Chem.* **24**, 2179 (1985).
5. L.D. Schultz, and G.R. Dobson, *J. Organomet. Chem.* **124**, 19 (1976).
6. G.R. Dobson, and L.D. Schultz, *J. Organomet. Chem.* **131**, 285 (1977).
7. For η^2-DTNW(CO)$_4$, the k_{obsd}/k'_{obsd} ratio is close to unity and the form of the rate-law is dependent on the size of L (reference [3]). For example, for the reaction of η^2-DTNW(CO)$_4$ with the non-bulky L (L = 4-methyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane (cone angle = 101°)) the non-steady-state intermediate *cis*-η^1-DTN(L)W(CO)$_4$ was observed and the biphasic behavior was observed, *i.e.*, k_{obsd}/k'_{obsd} ~ unity (reference [6]). For a ligand with a larger cone angle (L = P(OMe)$_3$, cone angle = 109°), the intermediate was not isolated but a curvature in the plot of $\ln(A_t - A_\infty)$ *vs.* time was observed. For large [P(OMe)$_3$] the curvature was concave

upward and for small $[P(OMe)_3]$ the curvature was concave downward (reference [3]). In such cases where the plot of $\ln(A_t - A_\infty)$ *vs.* time is slightly curved, the curvature is more commonly ascribed to small differences between the experimental value of A_∞ and the true value of A_∞ rather than to a biphasic process (J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, 2nd ed. (McGraw-Hill Book Co. New York, 1995) pp 71-75.). For still larger ligands such as $P(O\text{-}i\text{-}Pr)_3$ (cone angle = 130°) the value of $k'_{obsd} \gg k_{obsd}$ and the biphasic behavior was not observed (G.R. Dobson, S.S. Basson, and C.B. Dobson, *Inorg. Chim. Acta* **105**, L17 (1985).

8. G.M. Reisner, I. Bernal, and G.R. Dobson, *J. Organomet. Chem.* **157**, 23 (1978).
9. Shorter W-C and larger C-O bond distances for the carbonyls located at a *trans* position with respect to PDO were observed for η^2-PDOW(CO)$_4$. The *trans* influence was not observed for η^2-DTNW(CO)$_4$ and η^2-DTOW(CO)$_4$ complexes. J.E. Cortés-Figueroa, J.D. Subkowski, and E.J. Valente, *J. Chem. Cryst.* submitted (1997).
10. G. Illuminati, and L. Mandolini, *Acc. Chem. Res.* **14**, 95 (1981).
11. The complex exhibits distortion from the ideal octahedral geometry. However, the W-S1 and W-S2 bond distances are the same (2.545(3), 2.545(2) Å). The W-C bond distances located trans to PDO are the same within experimental error. The W-C bond distances located cis to PDO are also the same (reference 9).