

Octahedral Metal Carbonyls.

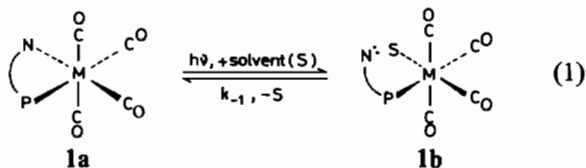
57*. Substituent, Ring-size and Metal Atom Effects on Chelate Ring-closure in $[(\eta^1\text{-Bidentate})\text{M}(\text{CO})_4]$ Intermediates ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$)

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Received January 4, 1985

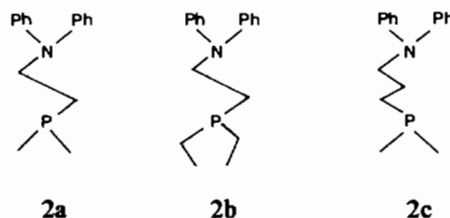
Pulsed laser flash photolytic methods recently have been employed in the determination of rates of chelate ring-closure in several $(\text{chelate})\text{M}(\text{CO})_4$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in organic solvents [2]. In particular, it has been found that bidentate ligands coordinating through a phosphorus and a nitrogen donor atom (NP), upon photolysis, undergo M-N bond fission to produce, *inter alia*, square-pyramidal $[(\eta^1\text{-NP})\text{M}(\text{CO})_4]$ intermediates (**1b**) which then can undergo chelate ring-closure with expulsion of solvent (see eqn. 1). Evidence indicates that such



photochemically generated intermediates are identical to those generated thermally [2d, 3]. For $(\text{chelate})\text{M}(\text{CO})_4$ complexes in which this anchoring phosphorus-containing group is the same save for a single substituent containing the coordinating nitrogen atom these intermediates are nearly identical. Thus the study of ring-closure in a series of such complexes would afford the opportunity to determine rates of ring-closure as a function of factors such as chelate ring-size and the identity of substituents bonded to coordinating N. Moreover, a comparison of rates of chelate ring closure as a function of the identity of the metal atom to known rates of M-L ($\text{L} = \text{Lewis base}$) bond fission [4] would provide useful information about the nature of intermediates (**1a**). Thus, rate constants and activation parameters for chelate ring-closure have been determined for the nine intermediates $[(\eta^1\text{-NP})\text{M}(\text{CO})_4]$, where NP = (**2a-2c**) and $\text{M} = \text{Cr}, \text{Mo}$ and W in order to investigate such influences.

*For Part 56, see ref. 1.

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Experimental

The bidentate ligands were synthesized through reaction of Ph_2PLi and $\text{Cl}(\text{CH}_2)_n\text{NR}_2$ ($n = 2, 3$; $\text{R} = \text{Me}, \text{Et}$) in dry THF [5]; the complexes were synthesized through use of standard thermal (for NP = **2a, 2b** [6]) or photochemical (NP = **2c** [7]) methods. For NP = (**2a**), $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ [8]; (**2b**), $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ [6] and (**2c**), $\text{M} = \text{Mo}$ [8] the complexes had been prepared previously. Pulsed laser flash photolysis studies were carried out as described earlier [2c] employing a Nd:YAG laser (355 nm irradiating frequency, 11 ns FWHI, 120 mJ maximum output energy) through flash photolysis of the substrates (**1a**) in chlorobenzene (CB) at various temperatures and monitoring the decay of the solvated intermediates (**1b**) thus generated in the visible spectrum (430–500 nm, depending upon the identity of the intermediate). That the changes in absorption monitored were due to chelate ring-closure and not some other process has been demonstrated in a detailed investigation of one of these intermediates, $[(\eta^1\text{-Et}_2\text{NCH}_2\text{CH}_2\text{PPh}_2)\text{Mo}(\text{CO})_4]$ [**2c**]. Rates of reaction at *ca.* 25 °C are presented in Table I; activation parameters calculated from data taken over a temperature range of 14–47 °C are presented in Table II. Limits of error for the rate constants for unimolecular ring-closure, k_{-1} , (1) are given in parentheses as the uncertainties of the last digit(s) of the cited value to one standard deviation.

TABLE I. Rates of Ring-closure for $[(\eta^1\text{-NP})\text{M}(\text{CO})_4]$ Intermediates in Chlorobenzene at *ca.* 25 °C.

NP	M	T (°C)	$10^{-6}k_{-1}$ (sec ⁻¹)
$\text{Me}_2\text{NC}_2\text{H}_4\text{PPh}_2$	Cr	26.1	2.50(26)
	Mo	26.1	1.10(5)
	W	25.1	0.138(3)
$\text{Me}_2\text{NC}_3\text{H}_6\text{PPh}_2$	Cr	26.1	0.222(4)
	Mo	25.2	0.0377(1)
	W	26.1	0.000391(4)
$\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2$	Cr	26.1	0.596(10)
	Mo	24.6	0.158(3)
	W	25.2	0.0187(5)

TABLE II. Activation Parameters for Ring-closure in $\{(\eta^1\text{-NP})\text{M}(\text{CO})_4\}$ Intermediates in Chlorobenzene.

NP	M	ΔH^* (kcal/mol)	ΔS^* (e.u.)
Me ₂ NC ₂ H ₄ PPh ₂	Cr	11.6(10)	9.6(34)
	Mo	7.5(6)	-5.8(20)
	W	10.5(2)	0.3(4)
Me ₂ NC ₃ H ₆ PPh ₂	Cr	13.75(2)	12.30(8)
	Mo	11.5(3)	1.3(8)
	W	12.1(24)	-1.4(63)
Et ₂ NC ₂ H ₄ PPh ₂	Cr	11.5(3)	6.8(10)
	Mo	8.7(8)	-4.0(17)
	W	10.50(2)	-3.53(8)

For the activation parameters, error limits based upon calculated values of k_{-1} are similarly defined.

Results and Discussion

The data (Tables I and II) show significant influences on the rates of chelate ring-closure of, (a) the identity of the metal atom; (b) chelate ring size and (c) the identity of the R groups bonded to the coordinating nitrogen atom.

(a) Rates of chelate ring-closure decrease in the order Cr > Mo >> W, although the corresponding enthalpies of activation vary Cr \approx W > Mo, an order similar to that observed for dissociation of CO and L (= amine) from Group VI-b metal carbonyl substrates [4]. This observation suggests, based upon Hammond's postulate [9], that the five-coordinate intermediates are quite similar in nature for the three metals. That anomalously rapid rates of reaction for the Cr intermediates are observed is attributable to more positive entropies of activation for them compared to those observed for the analogous Mo and W intermediates (Table II), perhaps the result of steric acceleration of solvent dissociation for the smaller Cr atom. This influence on reactivity is *not* observed for dissociative processes involving Group VI-b metal carbonyls and derivatives since desolvation takes place subsequent to the rate-determining step.

(b) Thermal displacement by L of chelating ligands has been observed to be accelerated for six-membered rings relative to five-membered rings in a number of (chelate)M(CO)₄ systems which have been investigated [10]. The data reported here, in contrast to an earlier interpretation [10a], suggest a significant influence of chelate ring-size on the rate of chelate ring-closure (a ten to thirty-fold increase in rate for the five-membered ring *vs.* the six-membered ring, Table I). This acceleration is largely due to an enthalpy effect, which has been attributed to greater dis-

tortion induced in the complex upon closure for a six-membered *vs.* a five-membered ring [11].

(c) A significant effect upon the rate of ring-closure is induced by changing the identity of R groups bonded to nitrogen (increases of as much as an order of magnitude when ethyl substituents are replaced by methyl groups), as might be anticipated on steric grounds.

Acknowledgements

The support of this research by the Robert A. Welch Foundation (Grant #B-434) and the North Texas State University Faculty Research Fund is gratefully acknowledged. The experiments and analyses of the pulsed laser flash photolysis data were performed at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Branch of the Division of Research Resources of the National Institutes of Health (RR000886) and by the University of Texas at Austin. We appreciate the experimental assistance and technical expertise of Dr. Stephen J. Atherton of the CFKR.

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