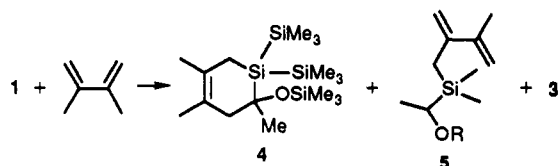


con-oxygen bonds.¹⁷ Whether the cyclic dioxasiletane adduct is formed awaits further study.¹⁸

Attempts to monitor reaction rates of 1 with well-known trapping agents such as dienes¹⁹ led to unexpected results. The rate of decay of the 330-nm signal was unchanged by increasing concentrations of 2,3-dimethylbutadiene (DMB) up to 0.33 M, indicating that the rate of silene addition to the diene is much slower than silene dimerization under flash photolytic conditions. Thus, k_t must be $\ll 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Continuous lamp ($\lambda_{\text{max}} = 350 \text{ nm}$, 20 m) photolysis of a cyclohexane solution of 2 (21.2 mM) and the diene (0.0, 0.2, 0.4, and 0.8 M) in a Rayonet-type reactor yielded products both from silene dimerization (3) and from reaction with DMB (4 and 5). Yields are summarized in Table II.



For this reaction the steady-state approximation (eq 1) may be used in combination with the expression relating the ratio of the rate constants to the ratio of products yields (eq 2) to arrive at eq 3. Thus, from a plot of the

$$d[1]/dt = 0 = \phi I_0 - 2k_t[1]^2 - k_r[1][\text{DMB}] \quad (1)$$

$$2k_t[1]^2/k_r[1][\text{DMB}] = R \quad R = [3]/([4] + [5]) \quad (2)$$

$$\sqrt{2k_t\phi I_0/R(R+1)} = k_r[\text{DMB}] \quad (3)$$

values of the left side of eq 3, which depends on the ratio of products, $R = [3]/([4] + [5])$, against the diene concentration, a straight line is obtained. The slope is to be equated to the composite rate constant, k_r , for the reaction of 1 with 2,3-DMB.

Interestingly, examination of eq 3 clearly reveals that low values of R (i.e. efficient diene trapping) can be expected only at low light intensities (I_0), thus explaining why addition products are observed from lamp irradiation but not in the flash irradiation and, also, the observation that the transient decays remain second order even in the presence high concentrations of the diene.

The composite rate constant is the sum of the individual rate constants for the 2 + 4 cycloaddition producing 4 and the "ene" pathway producing 5. For these pathways the ratio of rates equals the ratio of the product yields in eq 4.

$$k_{\text{ene}}/k_{2+4} = [4][5] \quad k_r = k_{2+4} + k_{\text{ene}} \quad (4)$$

$$k_{2+4} = k_r/([4][5]^{-1} + 1)$$

Thus we find that $k_{\text{ene}} \approx 0.04 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{2+4} \approx 0.19 \text{ M}^{-1} \text{ s}^{-1}$. These rate constants are small and consistent with the results of the flash photolysis experiments.

Acknowledgment. R.T.C. gratefully acknowledges financial support from the R. A. Welch Foundation. J.C.S. acknowledges support from the National Science and Engineering Research Council of Canada.

OM910619X

(17) Bellamy, L. J. *Advances in Infrared Group Frequencies*; Chapman Hall: London, 1975.

(18) It has been suggested in ref 1 that reaction between the 1,1-bis(trimethylsilyl)-2-adamantylsilene and O_2 produced an unstable dioxasiletane that fragmented to a ketone and bis(trimethylsilyl)silanone, which subsequently cyclotrimerized.

(19) Brook, A. G.; Vorspohl, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* 1987, 6, 2128.

Thermal Ring Closure in $\text{Mo}(\text{CO})_5\text{L}$ (L = bpy, dmbpy, dpbpy) Transients Generated by Pulsed Laser Flash Photolysis. Mechanistic Information from High-Pressure Effects

Kedika Bal Reddy, Rüdiger Hoffmann, Gabor Konya, Rudi van Eldik,*[†] and Edward M. Eyring*

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

Received January 28, 1992

Summary: The kinetics of the ring-closure reactions of $\text{Mo}(\text{CO})_5\text{L}$, produced during the laser flash photolysis of $\text{Mo}(\text{CO})_6$ and L where L = 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy) and 4,4'-diphenyl-2,2'-bipyridine (dpbpy) were studied as a function of temperature and pressure. The values of the activation parameters ΔS^\ddagger and ΔV^\ddagger are small and negative for L = bpy and dmbpy supporting an associative interchange mechanism (I_a) for CO extrusion. For L = dpbpy, ΔV^\ddagger is small and positive in line with a dissociative interchange mechanism (I_d). The results demonstrate a changeover in mechanism from I_a to I_d with increasing steric hindrance on the bidentate ligand L.

[†]Institute for Inorganic Chemistry, University of Witten/Herdecke, 5810 Witten, Germany.

There have been a number of pulsed laser flash photolysis studies of group VIb metal carbonyls in recent years.¹⁻⁸ Much attention has been focused on understanding the mechanistic behavior of coordinatively unsaturated intermediates produced after M-CO bond fission during photolysis because of the important applications of $\text{M}(\text{CO})_5\text{S}$ species in the area of systematic organometallic synthesis and the design of homogeneous catalysts.⁹⁻¹⁴ Application of high-pressure kinetic techniques

(1) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* 1981, 20, 4381.

(2) Oishi, S. *Organometallics* 1988, 7, 1237.

(3) Kalayanasundaram, K. *J. Phys. Chem.* 1988, 92, 2219.

(4) Wang, Li; Zhu, X.; Spears, K. G. *J. Am. Chem. Soc.* 1988, 110, 8695.

(5) Joly, A. G.; Nelson, K. A. *J. Phys. Chem.* 1989, 93, 2876.

(6) Zhang, S.; Dobson, G. R. *Inorg. Chim. Acta* 1989, 165, 111.

(7) Dobson, G. R.; Spradling, M. D. *Inorg. Chem.* 1990, 29, 880.

(8) Zhang, S.; Dobson, G. R. *J. Coord. Chem.* 1990, 21, 155.

in mechanistic studies of inorganic and organometallic systems has in general contributed significantly to a better understanding of ligand substitution processes.¹⁵⁻¹⁸ Recently, high-pressure techniques have been applied with success in combination with laser flash photolysis¹⁹⁻²³ and pulse radiolysis.²⁴

For group VIb metal complexes volumes of activation (ΔV^\ddagger) for CO displacement reactions, in general, are known to decrease from Cr to Mo and W. This decrease was attributed to a gradual changeover in mechanism from a more dissociative (D or I_d) mechanism for the smaller Cr to a more associative (A or I_a) type of mechanism for the larger Mo and W metal centers.^{22,25} A changeover was previously observed for the chelation reactions of Cr carbonyl complexes,²⁶ where the ring-closure of a bulkier chelating ligand (such as 1,4-diisopropyl-1,4-diazabutadiene) occurs by a dissociative (D) mechanism but the ring-closure of a smaller chelating ligand (such as ethylenediamine) occurs in an associative (A) way. For some CO displacement reactions the Mo complexes exhibited a borderline behavior between that of the corresponding Cr and W complexes.^{22,25} In this respect it is interesting to investigate whether ΔV^\ddagger for chelation reactions of Mo carbonyl complexes is sensitive to steric effects on the chelate ligand and whether a mechanistic changeover does occur on increasing the steric hindrance. We therefore investigated in the present study the rate and activation parameters (ΔH^\ddagger , ΔS^\ddagger , and ΔV^\ddagger) for chelate ring-closure in $\text{Mo}(\text{CO})_5\text{L}$ (L = 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), 4,4'-diphenyl-2,2'-bipyridine (dpbpy)) produced in situ after pulsed laser flash photolysis of $\text{Mo}(\text{CO})_6$ and L in toluene.

Experimental Section

$\text{Mo}(\text{CO})_6$ (Aldrich) was vacuum-sublimed before use. bpy (Aldrich) and dmbpy (Aldrich) were used without further purification. Technical grade dpbpy (Aldrich) was recrystallized twice from toluene. Toluene (Aldrich) was distilled from Na under a nitrogen atmosphere. All test solutions were prepared under a N_2 atmosphere using Schlenk techniques. The pulsed laser flash photolysis studies were carried out by employing a Quanta-Ray DCR-2 Nd:YAG laser operating at $\lambda = 355$ nm (100 mJ, 5-6-ns

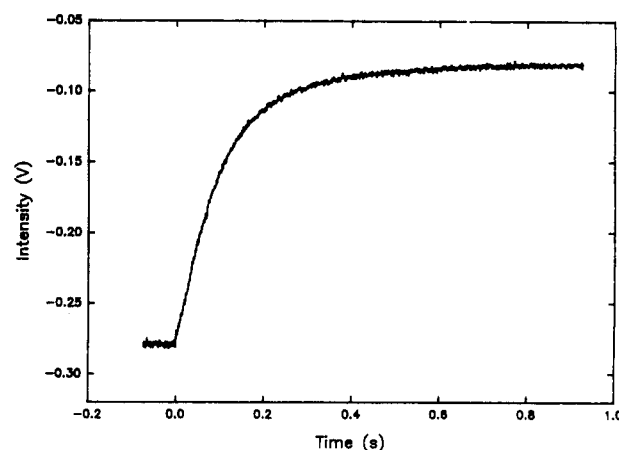
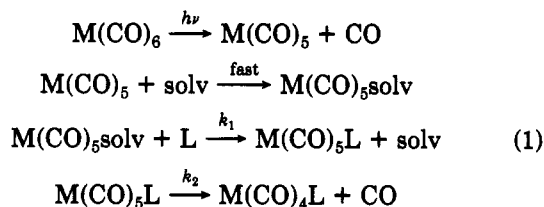


Figure 1. Typical kinetic trace monitored at $\lambda = 495$ nm for the reaction taking place after flash photolysis of $\text{Mo}(\text{CO})_6$ (0.002 M) and bpy (0.02 M) in toluene at 32 °C and ambient pressure.

whi). The system employed an Oriel 75-W xenon lamp as the analyzing source, a Durrum monochromator, and a Hamamatsu 1P28 photomultiplier detector. The photolysis beam intersected the observation beam at right angles in the high-pressure spectrophotometric cell.²⁷ 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 pump (heptane) was used for this purpose. A quartz pillbox sample cell²⁸ 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.²⁹ The signal was sent to a LeCroy 9400 oscilloscope interfaced (GPIB) to an IBM-compatible PC (Zenith). Data were analyzed by using a Turbo Pascal-based computer program developed in house. The first-order rate constants, k_{obs} , were obtained as averages of 5-10 kinetic traces. Volumes of activation were determined from the slopes ($-\Delta V^\ddagger/RT$) of the plots of $\ln k_{\text{obs}}$ versus P .

Results and Discussion

It is well-known that photolysis of $\text{M}(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) in the presence of L generates $\text{M}(\text{CO})_5\text{L}$.⁹ When L is a bidentate ligand, the primary photolysis product, $\text{M}(\text{CO})_5\text{L}$, undergoes a subsequent ring-closure reaction to produce $\text{M}(\text{CO})_4\text{L}$ and CO as shown in (1). The existence



of $\text{M}(\text{CO})_5\text{L}$ has been convincingly demonstrated earlier using a diode-array spectrophotometer and conventional techniques.³⁰⁻³⁴ The relative stability of $\text{M}(\text{CO})_5\text{L}$ depends on the nature of the metal center and the chelating ligand. During time-resolved studies of laser flash photolysis of $\text{M}(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) in the presence of diimine ligands (bpy and 1,10-phenanthroline (phen)), the half-life for the $\text{M}(\text{CO})_5\text{bpy}$ ($M = \text{Cr}, \text{Mo}, \text{W}$) ring-closure reaction was reported³ to be too slow for access by the fast kinetic

(27) Fleischman, F. K.; Conze, E. G.; Stranks, D. R.; Kelm, H. *Rev. Sci. Instrum.* 1971, 45, 1427.

(28) Le Noble, W. J.; Schlott, R. *Rev. Sci. Instrum.* 1976, 47, 770.

(29) Wieland, S.; van Eldik, R. *Rev. Sci. Instrum.* 1989, 60, 955.

(30) Schadt, M. J.; Gresalfi, N.; Lees, A. J. *J. Chem. Soc., Chem. Commun.* 1984, 505.

(31) Schadt, M. J.; Gresalfi, N. J.; Lees, A. J. *Inorg. Chem.* 1985, 24, 2942.

(32) Schadt, M. J.; Lees, A. J. *Inorg. Chem.* 1986, 25, 672.

(33) Marx, D. E.; Lees, A. J. *Inorg. Chem.* 1987, 26, 620.

(34) Drolet, D. P.; Chan, L.; Lees, A. J. *Organometallics* 1988, 7, 2502.

(9) Geoffrey, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

(10) Salmon, R. G. *Tetrahedron* 1983, 39, 485.

(11) Julliard, M.; Channon, M. *Chem. Rev.* 1983, 83, 425.

(12) Moggi, L.; Juris, A.; Sandrini, D.; Manfrin, M. F. *Rev. Chem. Intermed.* 1984, 5, 107.

(13) Henrici-Olive, G.; Olive, S. *Coordination and Catalysis*; Verlag Chemie: New York, 1977.

(14) Crabtree, R. H. *Chem. Rev.* 1985, 85, 245.

(15) van Eldik, R., Ed. *Inorganic High Pressure Chemistry: Kinetics and Mechanisms*; Elsevier: Amsterdam, 1986.

(16) Kotowski, M.; van Eldik, R. *Coord. Chem. Rev.* 1988, 93, 19.

(17) van Eldik, R.; Asano, T.; Le Noble, W. J. *Chem. Rev.* 1989, 89, 549.

(18) Weber, G. In *High Pressure Chemistry and Biochemistry*; van Eldik, R., Jonas, J., Eds.; NATO ASI C 197; Reidel: Dordrecht, 1987, p 401.

(19) Awad, H. H.; Dobson, G. R.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* 1987, 1839.

(20) Zhang, S.; Dobson, G. R.; Zang, V.; Bajaj, H. C.; van Eldik, R. *Inorg. Chem.* 1990, 29, 3476.

(21) Zhang, S.; Zang, V.; Dobson, G. R.; Bajaj, H. C.; van Eldik, R. *J. Organomet. Chem.* 1990, 397, 279.

(22) Zhang, S.; Zang, V.; Dobson, G. R.; van Eldik, R. *Inorg. Chem.* 1991, 30, 385.

(23) Taube, D. J.; Projahn, D.; van Eldik, R.; Magde, D.; Traylor, T. G. *J. Am. Chem. Soc.* 1990, 112, 6881.

(24) van Eldik, R.; Cohen, H.; Meshulam, A.; Meyerstein, D. *Inorg. Chem.* 1990, 29, 4156.

(25) Awad, H. H.; Dobson, C. B.; Dobson, G. R.; Leipoldt, J. G.; Schneider, K.; van Eldik, R.; Wood, H. E. *Inorg. Chem.* 1989, 28, 1654.

(26) Bal Reddy, K.; van Eldik, R. *Organometallics* 1990, 9, 1418.

Table I. Rate Constants and Activation Parameters for Chelate Ring Closure in Mo(CO)₅L Complexes in Toluene

L	T, °C	P, MPa	k _{obs} , s ⁻¹	ΔH [‡] , kJ mol ⁻¹	ΔS [‡] , J K ⁻¹ mol ⁻¹	ΔV [‡] , cm ³ mol ⁻¹	
bpy	15.0	0.1	1.34 ± 0.10	62 ± 1	-26 ± 0.5	-3.9 ± 0.6	
	20.0	0.1	1.96 ± 0.17				
	26.0	0.1	3.35 ± 0.18				
		5.0	3.44 ± 0.35				
		50.0	3.80 ± 0.31				
		100.0	4.02 ± 0.35				
		150.0	4.30 ± 0.22				
		32.0	0.1				5.94 ± 0.38
		37.0	0.1				8.71 ± 0.35
	dmbpy	15.0	0.1				1.02 ± 0.07
20.0		0.1	1.63 ± 0.08				
26.0		0.1	2.80 ± 0.17				
		5.0	2.85 ± 0.10				
		50.0	3.19 ± 0.30				
		100.0	3.62 ± 0.13				
		150.0	3.88 ± 0.08				
		32.0	0.1	4.77 ± 0.25			
		37.0	0.1	7.50 ± 0.20			
dpbpy		15.0	0.1	0.47 ± 0.02	69 ± 2	-4.0 ± 1.0	5.4 ± 0.5
	20.0	0.1	0.83 ± 0.04				
	26.0	0.1	1.92 ± 0.08				
		50.0	1.68 ± 0.04				
		100.0	1.54 ± 0.16				
		150.0	1.37 ± 0.07				
		32.0	0.1	2.36 ± 0.14			
		37.0	0.1	4.20 ± 0.24			

Table II. Summary of the Available Kinetic Data for Ring-Closure Reactions of Mo(CO)₅L Complexes^a

solvent	L	k ₂ at 25 °C, s ⁻¹	ΔH [‡] , kJ mol ⁻¹	ΔS [‡] , J K ⁻¹ mol ⁻¹	ΔV [‡] , cm ³ mol ⁻¹	ref
Tol	en	3.0 × 10 ⁻⁶	72 ± 7	-92 ± 22	-5.4 ± 0.8	26
Tol	dabR ₂	1.1 × 10 ⁻³	78 ± 5	-40 ± 17	-9.5 ± 0.4	26
Tol	dpbpy	1.4	69 ± 2	-4 ± 1	5.4 ± 0.5	<i>b</i>
Tol	dmbpy	2.6	65 ± 1	-20 ± 0.5	-5.6 ± 0.4	<i>b</i>
Tol	bpy	3.1	62 ± 1	-26 ± 0.5	-3.9 ± 0.6	<i>b</i>
FB	phen	1.1 × 10 ⁴	47 ± 2	-9 ± 7	-2.9 ± 0.2	22

^a Abbreviations used: Tol = toluene, FB = fluorobenzene, en = ethylenediamine, dabR₂ = 1,4-diisopropyl-1,4-diazabutadiene, phen = 1,10-phenanthroline. ^b This work.

spectroscopy used, i.e. $k_2 \ll k_1[L]$. Earlier studies^{3,30-34} were made 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.

The carbonyl extrusion from Mo(CO)₅L generated by laser flash photolysis was monitored by an increase in absorbance at the characteristic MLCT band of the Mo(CO)₄L complex. Figure 1 shows a typical kinetic trace recorded at 495 nm following the laser flash. k_{obs} was found to be independent of the L concentration over a 20-fold concentration range. Thus the chelate ring closure reaction obeys the rate law (2) where k_2 is the rate constant for

$$-d[\text{Mo}(\text{CO})_5(\text{L})]/dt = k_2[\text{Mo}(\text{CO})_5(\text{L})] \quad (2)$$

chelate ring-closure. Rate constants were measured as a function of temperature and pressure for different ligands L and are presented along with the associated activation parameters in Table I.

The results in Table I show that the rate of ring-closure of Mo(CO)₅L complexes follows the order bpy > dmbpy > dpbpy, in agreement with an earlier study of the corresponding W(CO)₅L complexes (L = bpy, dmbpy, dpbpy, *t*-Bubpy).³² Thus an increase in steric hindrance on the chelating ligand does significantly affect the rate of ring-closure. This trend is accompanied by a gradual increase in ΔH[‡] and a significant increase in ΔS[‡] toward more positive values. The ease of ring-closure is reflected in the ΔH[‡] data, whereas the trend in ΔS[‡] suggests a possible change in the nature of the transition state. The overall ΔS[‡] values are in agreement with an I_a mechanism, i.e. bond formation accompanied by Mo-CO bond cleavage. The ΔV[‡] values strongly support the trend in ΔS[‡] and

suggest a changeover in mechanism from I_a to I_d on increasing the steric hindrance on the bpy ligand. The introduction of two methyl substituents causes a minor decrease in ΔV[‡], whereas the introduction of two phenyl substituents causes an increase in ΔV[‡] of almost 10 cm³ mol⁻¹. The small absolute magnitude of ΔV[‡] is in good agreement with that typically found for interchange processes.¹⁷ Thus the positive ΔV[‡] value observed for L = dpbpy must arise as a result of more Mo-CO bond lengthening during the formation of the transition state due to steric congestion caused by the bulky phenyl substituents.

A summary of the available rate and activation parameters for ring-closure reactions of Mo(CO)₅L complexes (including only systems for which ΔV[‡] are available) is given in Table II. The systems have been ordered according to increasing k_2 values, which is accompanied by a steady decrease in ΔH[‡], 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 for en and dabR₂, but significantly smaller than for the phen complex. The latter trend is related to the rigidity of the phen ligand and intramolecular interactions between the uncoordinated site of the phen ligand and the Mo center in the ring-opened species.²² The ΔV[‡] value in the phen case is significantly more positive than for the other systems, with the exception of dpbpy, and in fact is close to zero. This indicates that we are dealing with a pure interchange mode in which volume changes associated with bond formation and bond breakage almost cancel out, although the overall value could favor an I_a mechanism. This is further supported

by the near-zero ΔS^\ddagger value found for the phen system. It is only in the case of the most sterically hindered dpbpy complex that a change in sign of ΔV^\ddagger really occurs; i.e. in this case the steric hindrance reaches a critical point where an associative (I_a) ring-closure is not possible anymore, and the reaction is forced to follow a dissociative (I_d) mechanism.

The present study demonstrates that a changeover in ring-closure mechanism from I_a to I_d is possible in the case of the Mo metal center when extreme steric hindrance on the chelating ligand is introduced. 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.²⁵ In addition, this has also more generally been observed for ligand substitution of group VIB metal carbonyl complexes in going from the larger W- to the smaller Mo- and Cr-centered complexes.^{21,22,26,35}

Thus the sizes of the metal center and of the coordinated and entering ligands play a crucial role in determining the location of the transition state along the reaction coordinate which involves bond cleavage with the leaving and bond formation with the entering nucleophile. Once again, the values of ΔV^\ddagger have demonstrated the informative nature of this activation parameter.³⁶

Acknowledgment. This work was supported in part by the Department of Energy, Office of Basic Energy Sciences (E.M.E.), and by the Deutsche Forschungsgemeinschaft (R.v.E.).

OM920043R

(35) Wieland, S.; van Eldik, R. *Organometallics* 1991, 10, 3110.

(36) van Eldik, R.; Merbach, A. E. *Comments Inorg. Chem.* 1992, 12, 341.

Additions and Corrections

Nathalie Le Berre-Cosquer, René Kergoat,* and Paul L'Haridon: Reaction of Vinylacetylene with $[Mo(\eta^5-C_5H_5)(CO)_2]_2$. Reactivity of $[Mo(\eta^5-C_5H_5)(CO)_2(\mu-HC\equiv CCH=CH_2)]$. Crystal Structures of $[Mo(\eta^5-C_5H_5)(CO)_2(\mu-\eta^2, \eta^3-HC\equiv CCHCH_3)][BF_4]$ and of $[Mo(\eta^5-C_5H_5)(CO)_2]_2(\mu-\mu-HC\equiv CCH_2CH_2)_2$. 1992, 11, 721-728.

The formula of the compound $[Mo(\eta^5-C_5H_5)(CO)_2(\mu-HC\equiv CCH=CH_2)]$ was written incorrectly in the original title.

William R. Cullen,* Steven J. Rettig, and Tu-cai Zheng: Thermolysis of $Ru_3(CO)_{10}[Fe(\eta-C_5H_4PPr^i)_2]_2$. Structure of $Ru_3(CO)_8(\mu-H)_2[(\eta-PC_5H_4)Fe(\eta-C_5H_4PPr^i)_2]$ and $Ru_3(CO)_8(\mu-Cl)(\mu-OH)[\mu-Fe(\eta-C_5H_4PPr^i)_2]_2$. 1992, 11, 853-858.

The title of this paper should appear as shown above.