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## BIMETALLIC COMPLEXES WITH BRIDGING DITHIAALKANE LIGANDS: PREPARATION AND KINETIC STUDY

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Reactions of  $M(\text{CO})_5\text{THF}$ , which was generated photochemically from  $M(\text{CO})_6$  in THF, with  $(\text{CH}_3)_3\text{CS}(\text{CH}_2)_n\text{SC}(\text{CH}_3)_3$  (=SS;  $n = 5, 6$ ;  $M = \text{W}, \text{Cr}$ ) at room temperature afforded exclusively the bimetallic complexes  $(\text{CO})_5\text{MSSM}(\text{CO})_5$ . These new complexes with dithiaalkane bridging ligands have been characterized by IR and  $^1\text{H NMR}$  spectroscopies and elemental analysis. Kinetic studies of ligand-exchange reactions in these complexes in chlorobenzene (=CB) solutions employing tri(*iso*-propyl)phosphite (=L) as an incoming nucleophile indicated that the bridging ligand SS is replaced by L to afford finally  $(\text{CO})_5\text{MP}(\text{O}-i\text{-Pr})_3$  as the sole reaction product. The kinetic data have also confirmed that replacement of SS by L under *pseudo*-first-order reaction conditions is dissociative and proceeds *via* a mechanism which involves initial M–S bond breaking followed by other steps. First order rate constants and activation parameters for these reactions have been determined.

*Keywords:* Metal carbonyls; Bimetallic; Sulfur bridging ligands; Kinetics; Mechanism; Substitution

### INTRODUCTION

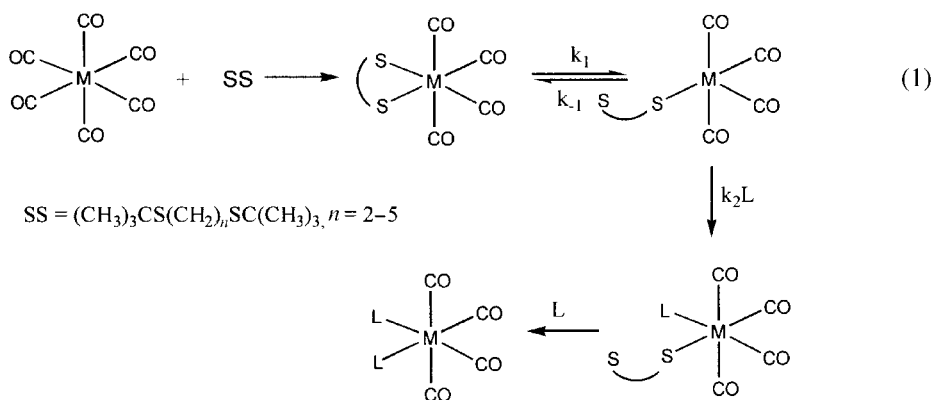
The substitution reactions of group VIB metal carbonyls ( $M(\text{CO})_6$ ,  $M = \text{Cr}, \text{Mo}, \text{W}$ ) with a large variety of nucleophiles, L, such as phosphines, phosphites, or amines, have been the subject of several reports [1]. The kinetics of these substitution reactions were also investigated [1]. Substitution reactions with bidentate ligands (LL), such as  $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ ,  $n = 1-5$ , have also been studied [2]. In general, formation of complexes of the type  $M(\text{CO})_4(\text{LL})$  is observed. Accordingly, a large number of such complexes have been prepared, characterized and their kinetics have been studied [2].

Several complexes where the bidentate ligand is dithiaalkane (SS:  $\text{RS}(\text{CH}_2)_n\text{SR}$ ),  $n = 1-5$ , have been prepared and their kinetics have been studied by Dobson and coworkers [3]. The displacement of these chelated ligands by phosphines or phosphites (=L) resulted initially in the formation of *cis*- $\text{L}_2\text{M}(\text{CO})_4$  *via* the intermediate *cis*-(L)

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$(\eta^1\text{-SS})\text{M}(\text{CO})_4$  which was observed spectroscopically. The complex  $\text{cis-}(\text{L}_2)\text{M}(\text{CO})_4$  may undergo, depending on the steric and electronic properties of L, subsequent isomerization to an equilibrium mixture containing also the *trans* isomer [4]. The rate constants for chelate-ring-opening ( $k_1$ ) have been found to increase dramatically with increasing ring size [3]. The rate constant for the ring-reclosure (governed by  $k_{-1}$ ) was also slower for the larger rings, i.e.  $n=4$  and 5 as compared to those with  $n=2$  and 3, Eq. (1). Thus the main influence on reactivity of chelated ring size was a dramatic increase in  $k_1$ , of about 7500-fold along the series  $n=2-5$ . However, for four-membered dithiaalkane ring complexes,  $n=1$ , it has been observed by Dobson and coworkers that the rate of ring-opening is faster compared to those with larger chelate complexes, and thus an associative type mechanism was proposed [3].



These results, suggested the possibility that for some dithiaalkane ligands with  $n \geq 4$ , it might be possible to prepare complexes in which SS ligands function as a “bridging” rather than a chelated ligand. Such expectation, with the absence of bimetallic complexes with bridging dithiaalkane ligands in the literature, prompted this study. In this paper, the preparation of bimetallic complexes of the type  $(\text{CO})_5\text{M}(\text{SS})\text{M}(\text{CO})_5$  ( $\text{M} = \text{Cr}, \text{W}$ ;  $\text{SS} = (\text{CH}_3)_3\text{CS}(\text{CH}_2)_n\text{SC}(\text{CH}_3)_3$ ,  $n = 5, 6$ ) is described. Ligand-exchange reactions of these SS bridging complexes with tri(*iso*-propyl)phosphite and their thermal kinetics data are also discussed.

## EXPERIMENTAL

All reactions were performed under an  $\text{N}_2$  atmosphere using Schlenk techniques [5]. Toluene, hexane and THF were dried and distilled over sodium and benzophenone. Chlorobenzene was used without further purification. The following chemicals: chromium hexacarbonyl, tungsten hexacarbonyl, dibromoalkanes, *tert*-butylmercaptan and tri(*iso*-propyl)phosphite, were used as purchased from Aldrich. The dithiaalkane ligands were prepared as described according to literature methods [3].

Infrared spectra were recorded on a Nicolet-Impact 410 FT-IR spectrometer.  $^1\text{H}$ NMR spectra were recorded using a Bruker, Advance DPX 300 MHz spectrometer. Elemental analyses were performed by M-H-W laboratories, Phoenix, Arizona, USA.

All photolytic experiments were carried out employing a medium pressure mercury lamp (150 W) with a quartz immersion cell purchased from Heraeus.

### General Procedure for the Preparation of $[M(CO)_5]_2(\mu\text{-SS})$

A solution of  $M(CO)_6$  (2.0 mmol) in THF was irradiated with UV light in a quartz photolysis vessel for about 2 h resulting in an orange solution of  $M(CO)_5$ THF. The ligand SS (1.0 mmol) in THF was added to this solution and the reaction mixture was stirred for one hour at room temperature. The resulting solution was filtered over Celite and the volatiles were removed under reduced pressure. The remaining residue was recrystallized from toluene/hexane (1:3 ratio) and the solution was kept overnight in a freezer. Yellow crystals of the products were collected by suction filtration and were washed with 20 mL of cold hexane.

$[W(CO)_5]_2(\mu\text{-}(CH_3)_3CS(CH_2)_5SC(CH_3)_3)$  (**1a**) Yield, 79%. m.p., 97–98°C. Anal. Calcd. for  $(C_{23}H_{28}O_{10}S_2W_2)$ : C, 30.82; H, 3.15. Found: C, 30.98; H, 3.45. IR (hexane,  $cm^{-1}$ ):  $\nu_{CO}$ : 2073 (w), 1942 (s), 1935 (s), 1929 (sh).  $^1H$  NMR ( $CDCl_3$ ): 1.41 (s, 18H,  $CH_3$ ), 1.55–1.66 (m, 2H,  $CH_2CH_2CH_2\text{-S}$ ), 1.78 (p, 4H,  $CH_2CH_2\text{-S}$ ), 2.88 (t, 4H,  $CH_2\text{-S}$ ).

$[W(CO)_5]_2(\mu\text{-}(CH_3)_3CS(CH_2)_6SC(CH_3)_3)$  (**1b**) Yield, 71%; m.p., 121–123°C. Anal. Calcd. for  $(C_{24}H_{30}O_{10}S_2W_2)$ : C, 31.67; H, 3.32. Found: C, 31.70; H, 3.41. IR (hexane,  $cm^{-1}$ ):  $\nu_{CO}$ : 2073 (w), 1942 (s), 1935 (s), 1928 (sh).  $^1H$  NMR ( $CDCl_3$ ): 1.41 (s, 18H,  $CH_3$ ), 1.49 (p, 4H,  $CH_2CH_2CH_2\text{-S}$ ), 1.74 (p, 4H,  $CH_2CH_2\text{-S}$ ), 2.87 (t, 4H,  $CH_2\text{-S}$ ).

$[Cr(CO)_5]_2(\mu\text{-}(CH_3)_3CS(CH_2)_5SC(CH_3)_3)$  (**2a**) Yield, 78%. m.p., 69–71°C. Anal. Calcd. for  $(C_{23}H_{28}O_{10}S_2Cr_2)$ : C, 43.67; H, 4.46. Found: C, 43.23; H, 4.23. IR (hexane,  $cm^{-1}$ ):  $\nu_{CO}$ : 2067 (w), 1946 (s), 1936 (s), 1931 (sh).  $^1H$  NMR ( $CDCl_3$ )  $\delta$ , ppm: 1.39 (s, 18H,  $CH_3$ ), 1.49–1.62 (m, 2H,  $CH_2CH_2CH_2S$ ), 1.76 (p, 4H,  $CH_2CH_2S$ ), 2.67 (t, 4H,  $CH_2S$ ).

$[Cr(CO)_5]_2(\mu\text{-}(CH_3)_3CS(CH_2)_6SC(CH_3)_3)$  (**2b**) Yield, 70%. m.p., 108–110°C. Anal. Calcd. for  $(C_{24}H_{30}O_{10}S_2Cr_2)$ : C, 44.58; H, 4.68. Found: C, 44.20; H, 4.47. IR (hexane,  $cm^{-1}$ ):  $\nu_{CO}$ : 2067 (w), 1946 (s), 1937 (s), 1930 (sh).  $^1H$  NMR ( $CDCl_3$ )  $\delta$ , ppm: 1.39 (s, 18H,  $CH_3$ ), 1.43–1.52 (m, 4H,  $CH_2CH_2CH_2S$ ), 1.68–1.77 (m, 4H,  $CH_2CH_2S$ ), 2.67 (t, 4H,  $CH_2S$ ).

### Kinetic Studies

The kinetics of the thermal reactions were carried out under nitrogen in sealed glass cells maintained at constant temperature ( $\pm 0.1^\circ C$ ) employing a thermostated bath. The cells were kept in the dark and were removed from the bath for about 15 s while the absorbance value were being determined. Kinetic data were collected by following the decrease in absorbance of the substrates  $[M(CO)_5]_2(\mu\text{-SS})$  at 420 nm. At this wavelength the colorless reaction product,  $M(CO)_5L$ , did not absorb, and the absorbance of ligand-solvent blank,  $A_{\text{blk}}$ , could be substituted for the absorbance at infinite time  $A_\infty$ . Substrate concentration of *ca.*  $5.0 \times 10^{-4}$  M, and *pseudo*-first-order conditions

TABLE I Rate constants and activation parameters for the reaction of  $[(\text{CO})_5\text{M}]_2(\mu\text{-SS})$  complexes with  $\text{P}(\text{O-}i\text{-Pr})_3$  in CB at various temperatures to afford  $(\text{CO})_5\text{M}(\text{P}(\text{O-}i\text{-Pr})_3)$  products

<i>M</i>	SS	<i>T</i> , °C	$[\text{P}(\text{O-}i\text{-Pr})_3]$	$10^4 k_{\text{obsd}}$ , s <sup>-1</sup>	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , cal/mol·K	
Cr	DTDD <sup>a</sup>	25.0	0.06723	0.832(3)	23.0(2)	0.7(5)	
			0.08644	0.835(24)			
			0.04321	3.17(5)			
		35.0	0.05762	3.01(3)			
			0.06723	3.12(3)			
			0.03841	10.16(8)			
			0.04762	10.07(6)			
			45.0	0.0723			10.32(9)
W	DTDD	64.0	0.06243	0.81(2)	25.3(7)	-2(2)	
			0.07683	0.734(9)			
			0.09124	0.794(14)			
		72.0	0.06243	1.91(3)			
			0.07203	1.94(4)			
			0.09604	2.01(6)			
			0.04802	4.38(6)			
		80.0	0.07203	4.32(12)			
			0.09028	5.23(7)			
W	DTUD <sup>b</sup>	64.0	0.01921	0.921(18)	24.5(1)	-4(3)	
			0.03073	0.881(18)			
			0.04321	0.927(12)			
			0.06146	0.975(12)			
			0.01921	2.26(6)			
		72.0	0.0307	2.34(9)			
			0.04226	2.40(6)			
			0.05666	2.48(4)			
			0.07299	2.52(5)			
			0.0307	5.33(7)			
		80.0	0.04321	4.87(4)			
			0.06146	4.98(6)			
			0.09028	5.23(7)			

a = 2,2,11,11-Tetramethyl-3,10-dithiadodecane,  $(\text{CH}_3)_3\text{CS}(\text{CH}_2)_6\text{SC}(\text{CH}_3)_3$ ; b = 2,2,10,10-Tetramethyl-3,9-dithiaundecane,  $(\text{CH}_3)_3\text{CS}(\text{CH}_2)_5\text{SC}(\text{CH}_3)_3$ .

were attained through use of at least 20-fold excess of the incoming nucleophile,  $\text{P}(\text{O-}i\text{-Pr})_3$ , in chlorobenzene solutions.

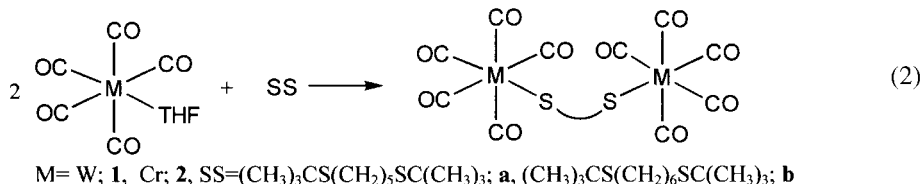
Plots of  $\ln(A_t - A_{\text{blk}})$  vs. time ( $A_t$  and  $A_{\text{blk}}$  are the absorbances at time  $t$  and that of ligand-solvent blank, respectively) were linear to at least three or more half-lives. Data were analyzed employing a linear-least-squares fitting program. Values for the *pseudo*-first-order rate constants are presented in Table I. Error limits are given in parentheses as the uncertainty of the last digit(s) cited to one standard deviation. Activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were determined from Eyring plots.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Complexes

The reaction of  $\text{M}(\text{CO})_5\text{THF}$  with SS ligands in 2:1 molar ratio in THF solution afforded the bridged complexes,  $[\text{M}(\text{CO})_5]_2(\mu\text{-SS})$ ,  $\text{SS} = (\text{CH}_3)_3\text{CS}(\text{CH}_2)_n\text{SC}(\text{CH}_3)_3$ ,

(M = W (**1**), Cr (**2**);  $n = 5$  (**a**),  $n = 6$  (**b**)) in good yields, Eq. (2),

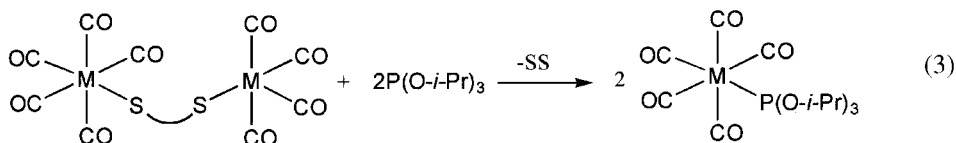


The progress of these reactions was monitored by following the disappearance of the stretching frequencies ( $\nu_{\text{CO}}$ ) of M(CO)<sub>5</sub>THF (M = Cr; 2070, 1936, 1893 cm<sup>-1</sup>, M = W; 2073, 1930, 1890 cm<sup>-1</sup>). The newly prepared compounds, **1** and **2**, are yellow crystals, air-stable as solids and soluble in organic solvents such as, hexane, THF and diethyl ether. These complexes were characterized on the basis of their IR and <sup>1</sup>HNMR spectra and elemental analysis.

The IR spectra of compounds **1** and **2** in hexane solution exhibit three bands in the ranges 2067–2073, 1942–1946 and 1935–1937 cm<sup>-1</sup>, which are indicative of the presence of the M(CO)<sub>5</sub> moieties [6]. Very weak bands in the range 1977–1981 cm<sup>-1</sup> were also observed [7]. The <sup>1</sup>HNMR spectra of compounds **1** and **2** exhibit signals which are in good agreement with the proposed structures. All chemical shift values of the protons appear in the expected region. However, a slight shift to lower field compared to those of the free ligands by 0.1–0.3 ppm upon coordination was observed [8].

### Kinetic Studies of the Displacement of SS by P(O-*i*-Pr)<sub>3</sub> from [M(CO)<sub>5</sub>]<sub>2</sub>(μ-SS)

Kinetics of the thermal reactions of [M(CO)<sub>5</sub>]<sub>2</sub>(μ-SS) in the presence of a large excess of P(O-*i*-Pr)<sub>3</sub> in CB solution were monitored at 420 nm, Eq. (3),



The *pseudo*-first-order rate constants,  $k_{\text{obsd}}$ , determined from the slopes of the plots of  $\ln(A_t - A_{\text{blk}})$  vs. time as illustrated in Fig. 1, exhibit linear relationships over a period of at least four half-lives. Values of  $k_{\text{obsd}}$  for these reactions at different temperatures are given in Table I. Thermal kinetic studies indicated that these ligand-exchange reactions are independent of the ligand (P(O-*i*-Pr)<sub>3</sub>) concentration, and obey a *pseudo*-first-order rate law:

$$-\frac{d[\text{M'SSM}']}{dt} = k_{\text{obsd}}[\text{M'SSM}'] \quad (4)$$

The mechanism can be represented by two reversible steps. The first step involves a reversible dissociation of one end of the SS ligand and is governed by  $k_1$  and  $k_{-1}$ , while the second step involves a reversible dissociation of the other end of SS ligand and is governed by  $k_3$  and  $k_{-3}$ . Both steps will generate the intermediate M(CO)<sub>5</sub>, which

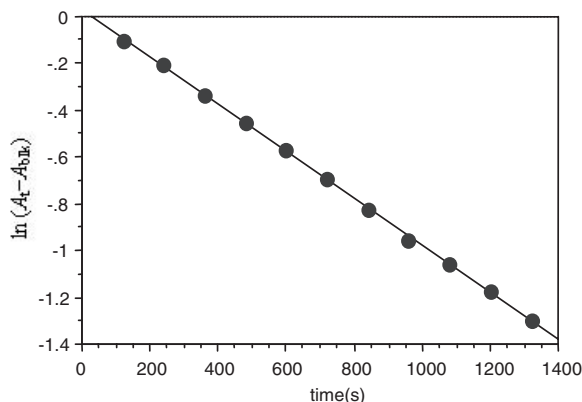
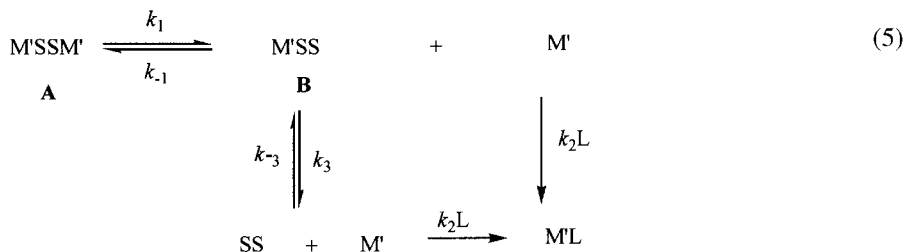


FIGURE 1 Plot of  $\ln(A_t - A_{bk})$  vs time for the reaction of  $[(CO)_5Cr_2(\mu-DTDD)]$  with  $P(O-i-Pr)_3$  (0.05762 M) at 45.0 °C monitored at 420 nm in CB.

reacts very rapidly with the incoming nucleophile  $L = P(O-i-Pr)_3$  to afford finally the reaction product as given in Eq. (5) [9],



$M' = M(CO)_5$ ;  $L = P(O-i-Pr)_3$ ;  $SS = (CH_3)_3CS(CH_2)_nSC(CH_3)_3$ ,  $n = 5$  and  $6$

For this mechanism, assuming that  $M'$  ( $= M(CO)_5$ ) to be a steady-state intermediate, the rate laws for the consecutive steps can be expressed in terms of disappearance of the substrates  $M'SSM'$  ( $= A$ ) and  $M'SS$  ( $= B$ ) respectively, for each step as follows:

$$\frac{-d[A]}{dt} = \frac{k_1k_{-3}[A][SS] + 2k_1k_2[A][L] - k_{-1}k_3[B]^2}{k_{-1}[B] + k_{-3}[SS] + 2k_2[L]} \quad (6)$$

$$\frac{d[B]}{dt} = \frac{2k_2k_{-3}[A][SS] + 2k_1k_2[B][L] - 2k_3k_2[B][L] - 2k_{-1}k_3[B]^2}{k_{-1}[B] + k_{-3}[A] + 2k_2[L]} \quad (7)$$

Each of these expressions can be simplified according to the applicable conditions. For the first expression (given in Eq. 6), taking into consideration that a large excess of the incoming nucleophile,  $(P-O-i-Pr)_3$ , was employed to ensure *pseudo*-first-order kinetics, and thus  $[L] \gg [A]$ ,  $[B]$ ,  $[SS]$ , the following approximations must

hold:  $2k_1k_2 [\mathbf{A}] [\mathbf{L}] \gg k_1k_{-3} [\mathbf{SS}] [\mathbf{A}]$ ,  $k_{-1} k_3[\mathbf{B}]^2$ , and  $2k_2 [\mathbf{L}] \gg k_{-1} [\mathbf{B}]$ ,  $k_{-3} [\mathbf{SS}]$ . Where these approximations are valid, then:

$$\frac{-d[\mathbf{A}]}{dt} = k_1[\mathbf{A}] \quad (8)$$

$$k_{\text{obsd}} = k_1 \quad (9)$$

It has been observed by several studies employing fast kinetics techniques that the process of solvation of intermediates of the type  $\text{M}(\text{CO})_5$ ;  $\text{M} = \text{Cr}, \text{W}$ , is extremely fast, and occurs in the picosecond time scale [10]. Thus, it is expected that both intermediates  $\text{M}'\text{SS}$  and  $\text{M}'$  exist initially as solvated species. However, it seems that there must be some rearrangement in the solvent cage so as to hinder the recombination of the fragments after bond fission. One more factor which will favor this assumption is the strong interaction between the coordinatively-unsaturated intermediate  $\text{M}(\text{CO})_5$  and CB solvent which involves  $\text{M}-\text{Cl}$  covalent bond formation [11]. Such interaction should be rather weak for the coordinatively-saturated complex  $\mathbf{B}$ . Thus, it is highly reasonable to assume that the intermediate  $\mathbf{B}$  diffuses from the solvent cage rather rapidly and reacts further by dissociating the other end of the ligand SS to afford the intermediate  $\text{M}(\text{CO})_5$ , which will react rapidly with the incoming nucleophile L to afford the reaction product  $\text{LM}(\text{CO})_5$ . Such a diffusion process will minimize the possibility of recombination of  $\mathbf{B}$  with  $\text{M}'$  (governed by  $k_{-1}$ ) in the solvent cage. Employing the same concept of approximation *vide supra* Eq. (7) thus becomes,

$$\frac{-d[\mathbf{B}]}{dt} = \frac{2k_1k_2[\mathbf{A}][\mathbf{L}] - 2k_3k_2[\mathbf{B}][\mathbf{L}]}{2k_2[\mathbf{L}]} = k_1[\mathbf{A}] - k_3[\mathbf{B}] \quad (10)$$

The amount of  $\mathbf{A}$  will be negligible at the end of the first portion of the reaction governed by  $k_1$ , thus  $k_3[\mathbf{B}] \gg k_1[\mathbf{A}]$  and the rate law for this second step should reduce to:

$$\frac{-d[\mathbf{B}]}{dt} = k_3[\mathbf{B}] \quad (11)$$

As previously stated, plots of  $\ln(A_t - A_{\text{blk}})$  vs. time were linear to more than 90% completion. Tentatively, it may be presumed that, based on statistical considerations, the value of  $k_1$  should be about twice that of  $k_3$ ; two  $\text{M}-\text{S}$  bonds to break in  $\text{M}'\text{SSM}'$  vs. one in  $\text{MSS}$ . The molar absorptivity of  $\text{M}'\text{SSM}'$  should also be about twice that of  $\text{M}'\text{SS}$  since the absorbing chromophore,  $\text{M}-\text{S}$ , in both species is the same, i.e. two in  $\text{M}'\text{SSM}'$  and one in  $\text{MSS}$ . That the rate constant as the reaction approaches  $t_\infty$  is the same as that near  $t_0$  and no curvature in the plots was observed, as expected if the absorbing species were different, would suggest that, unless some very fortuitous conditions are involved, this is the result of  $k_1$  and  $k_3$  being equal.<sup>1</sup> This is

<sup>1</sup>To justify this assumption, preliminary kinetics studies under similar reaction conditions to be communicated in another context, on complexes of the type  $(\text{CO})_5\text{M}-\text{SC}(\text{CH}_3)_3(\text{CH}_2)_n\text{CH}_3$ ,  $\text{M} = \text{W}, \text{Cr}$ ;  $n = 5$  and  $6$  which are comparable to  $\mathbf{B}$  has indicated that these complexes react with  $\text{P}(\text{O}-i\text{-Pr})_3$  under *pseudo*-first-order conditions with a rate law which is independent on the concentration of  $\text{P}(\text{O}-i\text{-Pr})_3$  and with a first order rate constant  $k_{\text{obsd}} = k_1$ , which is almost equivalent to  $k_1$  given in Eq. (5).



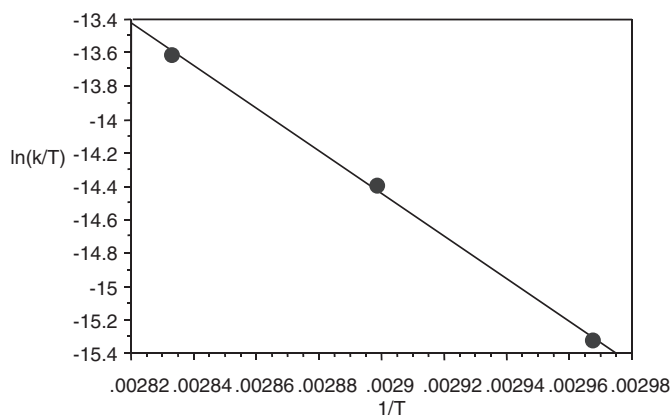


FIGURE 2 Eyring plot for the ligand substitution reaction of  $[(\text{CO})_5\text{W}]_2(\mu\text{-DTDD})$  with  $\text{P}(\text{O-}i\text{-Pr})_3$  at various temperatures.

reasonable in that the  $(\text{CH}_2)_n$  chains insulate the chromophore ends from the different “non-coordinating ends”. Besides, it is expected that there is high experimental uncertainty in  $k_3$  since this rate constant will dominate the rate law only after the starting species  $\text{M}'\text{SSM}'$  reaches a negligible concentration in solution.

First-order rate constants for these reactions and the activation parameters are presented in Table I. The Eyring plot for the ligand substitution reactions of  $[(\text{CO})_5\text{W}]_2(\mu\text{-DTDD})$  with  $\text{P}(\text{O-}i\text{-Pr})_3$  at various temperatures is shown in Fig. 2. Enthalpies of activation  $\Delta H^\ddagger$  determined through this study, given in Table I, should be comparable to M–S bond energies in these complexes, and are consistent with those obtained by Dobson and coworkers for W–S bond energies in the complex *cis*-(L)( $^1\eta$ -DTHp)W(CO)<sub>4</sub>, DTHp =  $(\text{CH}_3)_3\text{CSCH}_2\text{SC}(\text{CH}_3)_3$  [3]. It is evident from this study that increasing  $n$  in  $(\text{CH}_3)_3\text{CS}(\text{CH}_2)_n\text{SC}(\text{CH}_3)_3$  from  $n=5$  to 6 in these complexes did not significantly change the value of  $\Delta H^\ddagger$ . Entropies of activation ( $\text{M}=\text{Cr}$ ,  $n=6$ :  $\Delta S^\ddagger = 0.7(5)$  cal/mol·K;  $\text{M}=\text{W}$ ,  $n=6$ :  $\Delta S^\ddagger = -2(2)$  cal/mol·K,  $\text{M}=\text{W}$ ,  $n=5$ :  $\Delta S^\ddagger = -4(3)$  cal/mol·K), while not highly positive as expected for a dissociative mechanism, are consistent with a mechanism which involves solvent interaction during metal–ligand bond breaking while attaining the transition state. It is well established that various solvents interact with group VIB metal carbonyl unsaturated transients to form  $\text{M}(\text{CO})_5(\text{solvent})$  or  $\text{M}(\text{CO})_4(\text{L})(\text{solvent})$ ; solvent = alkanes or chlorinated hydrocarbons [11]. Thus, it is expected that the transient  $\text{W}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_5$  which will be generated in both reversible steps in Eq. (5), *vide supra*, will be stabilized in chlorobenzene solutions through the formation of a Cl–M coordinate bond [11,12].

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