

SYNTHESIS AND REACTIVITY OF GROUP 6 PENTACARBONYL DIALKYL SULFIDE COMPLEXES

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Abstract

Reactions of $M(\text{CO})_5\text{THF}$, which was generated photochemically from $M(\text{CO})_6$ in THF, with ${}^t\text{Bu-SR}$ ($R = (\text{CH}_2)_4\text{CH}_3, (\text{CH}_2)_5\text{CH}_3$; $M = \text{W}, \text{Cr}$) at room temperature afforded exclusively $(\text{CO})_5M({}^t\text{Bu-SR})$ type complexes. These new complexes have been characterized by IR and elemental analysis. Ligand-substitution reactions of these complexes with tri(*isopropyl*)phosphite ($= \text{L}$) in chlorobenzene ($= \text{CB}$) solutions gave $(\text{CO})_5M(\text{P}(\text{O-}i\text{-Pr})_3)$ as the sole reaction product. A thermal kinetics study of these ligand-substitution reactions under pseudo-first-order conditions in CB solutions, confirmed that these reactions proceed *via a* mechanism which is first-order in substrate and zero-order in $\text{P}(\text{O-}i\text{-Pr})_3$ concentrations. Thus, a dissociative mechanism is proposed, which involves initial M-S bond breaking, followed by fast attack of the incoming nucleophile, L, at the resulting five-coordinate intermediate. Rate constants and activation parameters for these ligand substitution reactions have been determined and are discussed.

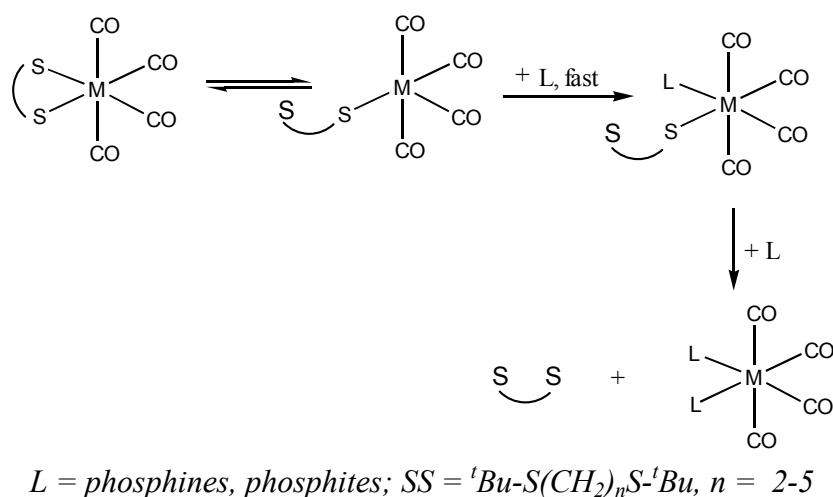
Keywords: Metal carbonyls, organic sulfide ligands, kinetics, mechanism.

Introduction

The kinetics and mechanism of the ligand-substitution reactions of group VIB chelated dithiaalkane complexes by phosphine or phosphite ligands have been widely studied.¹ These reactions proceed by a mechanism which involves initial reversible dissociation of one end of the chelated ligand to generate the unsaturated intermediate $(\eta^1\text{-SS})M(\text{CO})_4$ followed by fast attack of the incoming nucleophile, L, to give initially $(\eta^1\text{-SS})M(\text{CO})_4(\text{L})$, which reacts further with L to afford *cis*-(L)₂M(CO)₄ (Scheme 1). The *cis*- complex may undergo subsequent dissociative or nondissociative isomerization to give an equilibrium mixture of both the *cis*- and the *trans*-(L)₂M(CO)₄ isomers.²

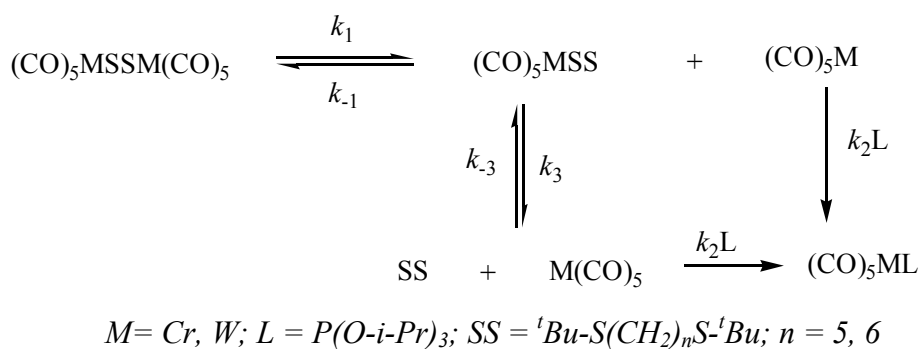
In a recent study, we prepared bimetallic complexes bridged by dithiaalkane ligands of the general formula $[\text{M}(\text{CO})_5]_2(\mu\text{-SS})$ ($\text{SS} = {}^t\text{Bu-S}(\text{CH}_2)_n\text{S-}{}^t\text{Bu}$, $n = 5$ for 2,2,10,10-tetramethyl-3,9-dithiaundecane (*DTUD*); $n = 6$ for 2,2,11,11-tetramethyl-3,10-dithiadodecane (*DTDD*)).³ A thermal kinetic study of the replacement of the bridging SS ligands from these complexes by tri(*isopropyl*)phosphite ($= \text{L}$) under pseudo-first-order conditions has indicated that these reactions proceed by a mechanism, which is

independent of the concentrations of L, and gave finally $\text{LM}(\text{CO})_5$ as the sole reaction product. Thus, a two-steps mechanism, which generates $\text{M}(\text{CO})_5$ intermediate in solution, was proposed (Scheme 2). The first step involves an initial reversible dissociation of one end of the bridging SS ligand, governed by k_1 and k_{-1} , and thus affords two mononuclear intermediates; namely, a saturated species $(\text{CO})_5\text{M}(\eta^1\text{-SS})$, and the unsaturated $\text{M}(\text{CO})_5$ intermediate. The second step involves a subsequent reversible dissociation of the other coordinated end of SS, governed by k_3 and k_{-3} , which will also afford the same intermediate, $\text{M}(\text{CO})_5$, and the free SS ligand. The kinetic data, which was obtained from the previous study³ was explained in terms of $k_1 \approx k_3$, which implies that both $[\text{M}(\text{CO})_5]_2(\mu\text{-SS})$ and $(\text{CO})_5\text{M}(\eta^1\text{-SS})$ undergo M-S bond fission at comparable rates.³ However all attempts to isolate the complex $(\text{CO})_5\text{M}(\eta^1\text{-SS})$ were unsuccessful.



Scheme 1

Accordingly, it is of interest to prepare and study the kinetics of some complexes that resemble and exhibit similar bonding properties of the proposed saturated intermediate, $(\text{CO})_5\text{M}(\eta^1\text{-SS})$. This report describes the synthesis of the complexes $(\text{CO})_5\text{M}({}^t\text{Bu-SR})$ ($M = \text{W, Cr}; R = -(\text{CH}_2)_4\text{CH}_3, -(\text{CH}_2)_5\text{CH}_3$), and the results of the thermal kinetics of the displacement of ${}^t\text{Bu-SR}$ ligands from these complexes by $\text{P}(\text{O-}i\text{-Pr})_3$.

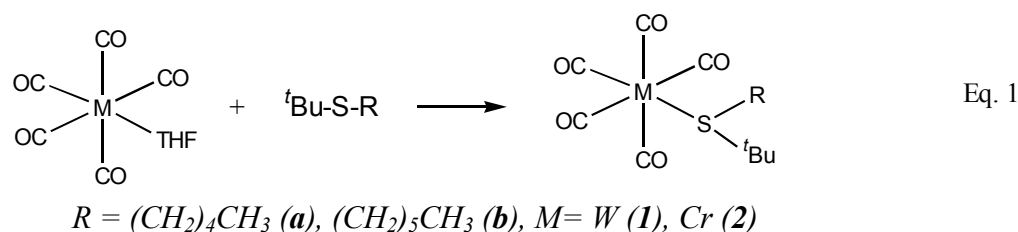


Scheme 2

Results And Discussion

Synthesis and characterization of complexes

The reaction of the photogenerated intermediate $\text{M}(\text{CO})_5\text{THF}$ with ${}^t\text{Bu-S}(\text{CH}_2)_n\text{CH}_3$ ($n = 4, 5$) at ambient temperatures in THF solutions afforded exclusively $\text{M}(\text{CO})_5({}^t\text{Bu-SR})$ ($M = \text{W}$ (**1**), Cr (**2**); $n = 4$ (**a**), $n = 5$ (**b**)) in good yields (Equation 1).

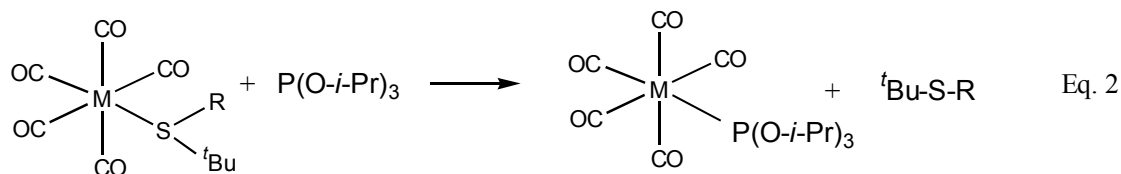


Compounds, **1** and **2**, are lemon yellow. They are soluble in most common organic solvents such as, hexane, THF and Et_2O . These complexes were characterized on the basis of their IR spectra and elemental analysis.

The IR spectra in the carbonyl stretching frequencies region of the complexes **1a**, **1b**, **2a**, and **2b** in hexane solution exhibit the typical three ν_{CO} bands in the ranges 2073–2067 (w), 1939–1940 (vs) and 1929–1932 (s) cm^{-1} , which are indicative of the presence of the $\text{M}(\text{CO})_5$ moieties.⁴ These bands are similar to those observed in comparable complexes.

Kinetic Studies of Reactions of $M(\text{CO})_5(^t\text{Bu-SR})$ with $P(\text{O-}i\text{-Pr})_3$

Kinetic studies of the thermal reactions of $M(\text{CO})_5(^t\text{Bu-SR})$ in the presence of large excess of $P(\text{O-}i\text{-Pr})_3$ in CB solution were employed (Equation 2).

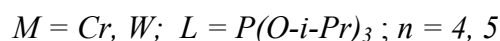
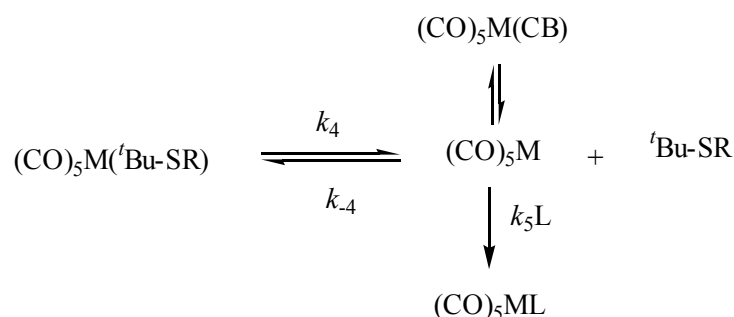


The reaction products of these ligand-substitution reactions, $M(\text{CO})_5(P(\text{O-}i\text{-Pr})_3)$, were identified by their characteristic carbonyl stretching frequencies as reported in the literature.^{5,6}

The pseudo-first-order rate constants, k_{obsd} , were determined from the slopes of the plots of $\ln(A_t - A_{\text{blk}})$ vs time (Figure 1), which exhibit linear relationship over a period of at least three half-lives. Values of k_{obsd} for these reactions are given in Table 1. The kinetic results indicate that these reactions are independent of $[P(\text{O-}i\text{-Pr})_3]$, and obey an observed rate law, shown in equation 3,

$$-d[(\text{CO})_5M(^t\text{Bu-SR})]/dt = k_{\text{obsd}}[(\text{CO})_5M(^t\text{Bu-SR})] \quad \text{Eq. 3}$$

A proposed stepwise mechanism is presented in Scheme 3.



Scheme 3

Assuming that $M(\text{CO})_5$ is a steady-state intermediate, the rate law for the disappearance of the substrate $M(\text{CO})_5^t\text{Bu-SR}$ is,

$$\text{Rate} = \frac{-d[(\text{CO})_5M(^t\text{Bu-SR})]}{dt} = \frac{k_4k_5[\text{L}][(\text{CO})_5M(^t\text{Bu-SR})]}{k_{-4}[^t\text{Bu-SR}] + k_5[\text{L}]} \quad \text{Eq. 4}$$

In terms of pseudo-first-order conditions, it is expected that $k_5[\text{L}] \gg k_{-4} [^t\text{Bu-SR}]$, Eq. 4 will reduce to

$$k_{\text{obsd}} = k_4 \quad \text{Eq. 5}$$

The observed first-order rate constants for these reactions and the activation parameters are presented in Table 1. The Eyring plot for the ligand-substitution reactions of $(\text{CO})_5W(^t\text{Bu-SR})$, $R = (\text{CH}_2)_5\text{CH}_3$, with $\text{P}(\text{O-}i\text{-Pr})_3$ at various temperatures is shown in Figure 2.

Values of k_{obs} obtained through this study are consistent with a mechanism which involves initial reversible dissociation of M-S bond, governed by k_4 and k_{-4} , followed by fast attack of the incoming ligand L at the resulting five-coordinated intermediate, $M(\text{CO})_5$, to afford the $M(\text{CO})_5(\text{P}(\text{O-}i\text{-Pr})_3)$ product. Besides, the k_{obs} values, which are a direct measure of k_4 *vide supra* are, within experimental error, equal k_1 and k_3 obtained for the ligand substitution reactions of the bridging dithiaalkane complexes, $[\text{M}(\text{CO})_5]_2(\text{DTA})$, Table 1, as illustrated in Scheme 2.³

Activation parameters: The activation parameters, ΔH^\ddagger and ΔS^\ddagger , for ligand substitution in these complexes have been determined from Eyring plots. These activation parameters are: M= W, n = 4 (**1a**): $\Delta H^\ddagger = 26.1(5)$ kcal/mol.K, $\Delta S^\ddagger = 0.5(1.0)$ eu; n = 5 (**1b**): $\Delta H^\ddagger = 24.20(2)$ kcal/mol.K, $\Delta S^\ddagger = -4.8(3)$ eu; M = Cr, n = 4 (**2a**): $\Delta H^\ddagger = 23.3(2)$ kcal/mol.K, $\Delta S^\ddagger = 2.1(8)$ eu, n = 5 (**2b**): $\Delta H^\ddagger = 23.4(5)$ kcal/mol.K, $\Delta S^\ddagger = 2(2)$. That a dissociative mechanism is proposed for these ligand substitution reactions, it is expected that the enthalpies of activation determined in this study should closely approximate the M-S bond strength in these complexes. The values of ΔH^\ddagger obtained through this study are in good agreement with those reported for comparable systems,⁷ and also favorably agree with those obtained for ligand substitution reactions for the

corresponding bridging dithiaalkane complexes of the $[M(CO)_5]_2(\mu\text{-SS})$ type, (SS = DTDD and DTUD),³ as given in Table 1.

Entropies of activation, while not highly positive as expected for a dissociative mechanism, are consistent with a mechanism which involves solvent (= CB) interaction during metal-S bond breaking while attaining the transition state. It is thus envisaged that solvation-desolvation of the intermediate $M(CO)_5$ occurs during the ligand substitution reaction as illustrated in Scheme 3. It is well established that various solvents interact with group 6 metal carbonyl unsaturated transients to form in solution $M(CO)_5(\text{solvent})$ or $M(CO)_4(L)(\text{solvent})$; solvent = alkanes or chlorinated hydrocarbons.⁸⁻¹⁰ In this study, it is expected that the transients, $M(CO)_5$ will undergo fast solvation-desolvation prior to formation of the reaction product, $M(CO)_5(L)$. However, attack of the incoming ligand, $P(O\text{-}i\text{-Pr})_3$, takes place at the naked rather than the solvated $M(CO)_5$ transients, as confirmed by fast kinetic studies employing pulsed-laser flash photolysis.¹⁰

In conclusion, comparison of the rate constants and the activation parameters obtained through this study with those observed for the reactions of the dithiaalkane complexes of $[M(CO)_5]_2(\mu\text{-SS})$ type under similar reaction conditions (Scheme 2), confirms the assumption, *vide supra*, that the first order rate constants k_1 and k_3 are comparable in value, and also comparable to k_4 values.

Experimental

All reactions were performed under a N_2 atmosphere using Schlenk techniques.¹¹ THF, Et_2O and hexane were dried and distilled over sodium and benzophenone. The following chemicals: $Cr(CO)_6$, $W(CO)_6$, bromoalkanes, *tert*-butylmercaptan and tri(*isopropyl*)phosphite (Aldrich), chlorobenzene (Acros), were purified according to literature procedures.¹²

Infrared spectra were recorded on a Nicolet-Impact 410 FT-IR spectrometer. Elemental analyses were performed by the 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 (Hereus).

Preparation of Ligands

In a 250-mL three-neck flask equipped with a magnetic stirrer, reflux condenser, dropping funnel and nitrogen inlet, sodium metal (2.00 g, 87 mmol) was dissolved in 50 mL of absolute ethanol. To this solution *tert*-butyl mercaptan (7.83 g, 87 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 2 h. Bromoalkane (87 mmol) was added dropwise with stirring over a period of 20-30 minutes, and then filtered to remove the resulting NaBr. Ethanol was removed by distillation. The resulting oily product was collected by vacuum distillation.

^tBu-S(CH₂)₄CH₃: Yield ~50%. b.p= 180 °C (13 mmHg).

^tBu-S(CH₂)₅CH₃: Yield ~ 50%. b.p=200 °C (13 mmHg).

General Procedure for the Synthesis of M(CO)₅(^tBu -SR)

A solution of M(CO)₆ (2.84 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)₅THF. A THF solution of the ligand Bu^t-SR (2.84 mmol) was added to the M(CO)₅THF solution and the reaction mixture was stirred for about one hour at room temperature. The resulting solution was filtered over *Celite* and the volatiles were removed under reduced pressure, yielding an oily yellow residue. Cold diethyl ether (~ 15 mL) was added to this residue and the solution was filtered again over *Celite* to remove any unreacted M(CO)₆ or any decomposition product(s). Diethyl ether was removed under reduced pressure. Yellow solid product was formed upon standing in a freezer at -50 °C. The product was stored under N₂ atmosphere.

W(CO)₅^tBu-S(CH₂)₄CH₃ (1a): Yield ~ 70%. IR (hexane, cm⁻¹): ν_{CO}: 2073 (w), 1939 (vs), 1929 (s). Calcd. for C₁₄H₂₀O₅SW: C, 34.73%; H, 4.16. Found, C, 34.31; H, 4.45%.

W(CO)₅^tBu-(CH₂)₅CH₃ (1b): Yield ~ 71%. IR (hexane, cm⁻¹): ν_{CO}: 2073 (w), 1939 (vs), 1931 (s). Calcd. for C₁₅H₂₂O₅SW: C, 36.16%; H, 4.45. Found, C, 36.22%; H, 4.67%.

Cr(CO)₅^tBu-S(CH₂)₄CH₃ (2a): Yield ~ 80%. IR (hexane, cm⁻¹): ν_{CO}: 2067 (w), 1940 (vs), 1932 (s). Calcd. for C₁₄H₂₀O₅SCr: C, 47.72%; H, 5.72. Found, C, 47.20%; H, 5.52%.

$\text{Cr}(\text{CO})_5^t\text{Bu-S}(\text{CH}_2)_5\text{CH}_3$ (2b): Yield \sim 78%. IR (hexane, cm^{-1}): ν_{CO} : 2067 (w), 1940(vs), 1933(s). Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_5\text{SCr}$: C, 49.17%; H, 6.05%. Found, C, 49.56%; H, 5.97%.

Thermal Kinetic Studies. Thermal kinetic runs were carried out under nitrogen in sealed glass cells maintained at constant temperature (± 0.1 °C) employing a thermostated bath. The cells were kept in the dark, and were removed from the bath for about 15 seconds while the absorbance values were being determined. Kinetic data were collected by following the decrease in absorbance of the substrates $\text{M}(\text{CO})_5^t\text{Bu-SR}$ at 420 nm, at which wavelength the colorless reaction product, $\text{M}(\text{CO})_5(\text{P}(\text{O}-i\text{-Pr})_3)$, does not absorb. Thus, the absorbance of ligand-solvent blank, A_{blk} , was employed in lieu of the absorbance at infinite time A_∞ . Initial substrate concentrations of *ca.* 7.0×10^{-4} M were employed. Pseudo-first-order conditions were maintained in all kinetic runs through the use of at least 20-fold excess of $[\text{P}(\text{O}-i\text{-Pr})_3]$ vs. $[\text{M}(\text{CO})_5^t\text{Bu-SR}]$ in chlorobenzene solutions.

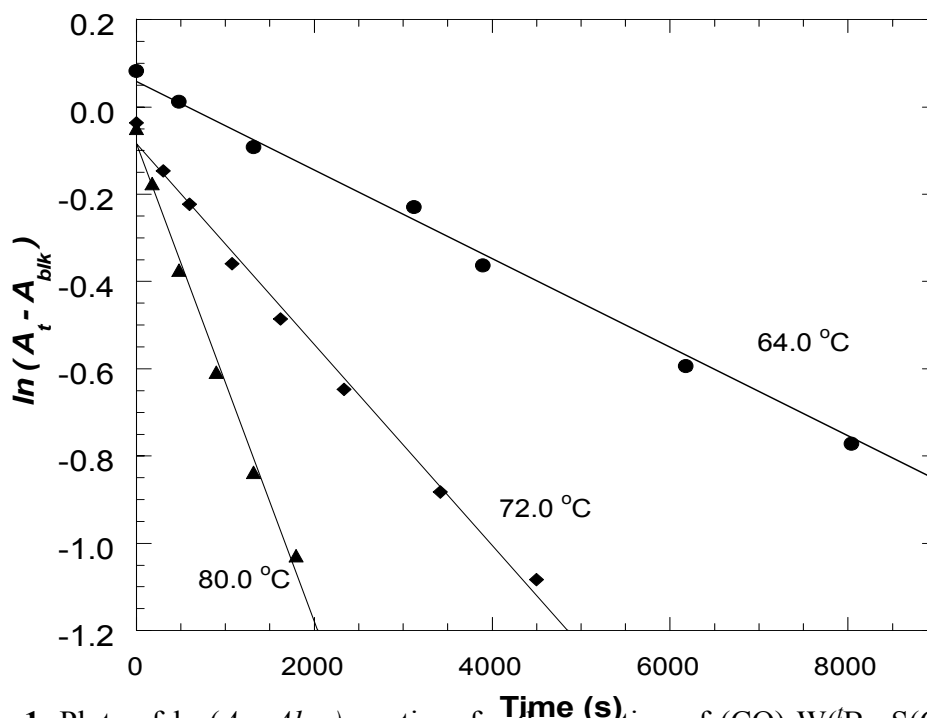


Figure 1. Plots of $\ln(A_t - A_{\text{blk}})$ vs time for the reaction of $(\text{CO})_5\text{W}^t\text{Bu-S}(\text{CH}_2)_5\text{CH}_3$ with $\text{P}(\text{O}-i\text{-Pr})_3$ at different temperatures in CB solutions.

Plots of $\ln(A_t - A_{blk})$ vs time (A_t and A_{blk} are the absorbances of the reaction solution at time t and of solvent-ligand blank, respectively) were linear to at least three or more half-lives. Data were analyzed employing a linear-least-squares fitting program. Limits of error, given in parentheses as the uncertainties of the last digit(s) of the experimental values, are one standard deviation. Values for the pseudo-first-order rate constants are presented in Table 1. Activation parameters ΔH^\ddagger and ΔS^\ddagger were determined from Eyring plots, and are also given in Table 1.

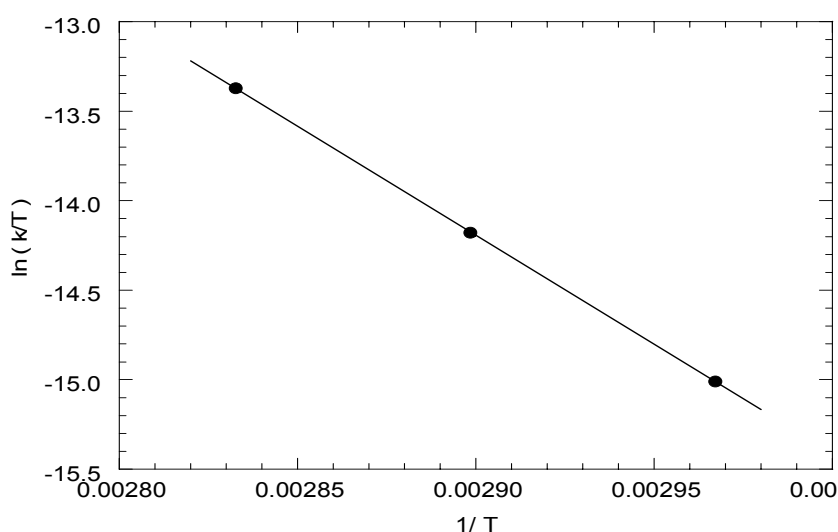


Figure 2. Eyring plot for the ligand substitution reaction of $(\text{CO})_5\text{W}(\text{}^t\text{Bu-S}(\text{CH}_2)_5\text{CH}_3)$ with $\text{P}(\text{O-}i\text{-Pr})_3$ in chlorobenzene solution.

Table 1. Rate Constants and Activation Parameters for the Reaction of the $[(\text{CO})_5\text{M}(\text{}^t\text{Bu-SR})]$ Complexes with $\text{P}(\text{O-}i\text{-Pr})_3$ ($= \text{L}$) in CB at Various Temperatures.

M	R	T, °C	L, M	$10^4 k_{\text{obsd}}$ (s^{-1})	ΔH^\ddagger kcal.mol $^{-1}$	ΔS^\ddagger (eu)
W	$-(\text{CH}_2)_4\text{CH}_3$	64.0	0.041	0.851(6)	26.1(5) ^a	0.5(1.0)
			0.077	0.882(2)		
			0.10	0.883(5)		
			0.19	0.865(1)		
		72.0	0.019	2.24(3)		
			0.081	2.50(5)		
		80.0	0.019	5.11(2)		
				5.44(8)		

Table 1 continued.

M	R	T, °C	L, M	$10^4 k_{\text{obsd}}$ (s ⁻¹)	ΔH^\ddagger kcal.mol ⁻¹	ΔS^\ddagger (eu)
	-(CH ₂) ₅ CH ₃	64.0	0.029 0.080	1.02(2) 1.03(2)	24.20(2) ^b	-4.8(3)
		72.0	0.080	2.62(4)		
			0.029	2.22(6)		
		80.0	0.080	5.48(2)		
Cr	-(CH ₂) ₄ CH ₃	27.0 35.0 45.0		1.32(2) 3.85(6) 12.80(2)	23.3(2)	2.1(8)
	-(CH ₂) ₅ CH ₃	27.0 35.0 45.0		1.107(2) 2.96(2) 10.70(4)	23.4(5) ^c	2(2)

^a For: [W(CO)₅]₂(DTUD) Reactions: $\Delta H^\ddagger = 24.5(1)$ kcal.mol⁻¹, $\Delta S^\ddagger = -4(3)$ eu.

^b For: [W(CO)₅]₂(DTDD) Reactions: $\Delta H^\ddagger = 25.3(7)$ kcal.mol⁻¹, $\Delta S^\ddagger = -2(2)$ eu.

^c For: [Cr(CO)₅]₂(DTDD) Reactions: $\Delta H^\ddagger = 23.0(2)$ kcal.mol⁻¹, $\Delta S^\ddagger = 0.7(5)$ eu.

DTUD = (CH₃)₃C-S-(CH₂)₅-S-C(CH₃)₃; DTDD = (CH₃)₃C-S-(CH₂)₆-S-C(CH₃)₃

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Povzetek

$M(CO)_5THF$, ki smo ga pripravili s fotokemično reakcijo iz $M(CO)_6$, tvori s $tBu-SR$ ($R = (CH_2)_4CH_3, (CH_2)_5CH_3$; $M = W, Cr$) izključno komplekse vrste $(CO)_5M(tBu-SR)$. Nove komplekse smo karakterizovali z IR spektroskopijo in elementno analizo. Študirali smo tudi reakcije zamenjave ligandov pri teh kompleksih. Predlagamo mehanizem izmenjave. Določili smo kinetične in termodinamične parametre teh reakcij.