SYNTHESIS AND LIGAND-SUBSTITUTION REACTIONS OF [Et₄N][M(CO)₅SCPh₃] (M = W, Mo)

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Abstract

The complexes $[Et_4N][M(CO)_5SCPh_3]$ (M = W, **1a**; Mo, **1b**) were prepared by the reaction of $[Et_4N][SCPh_3]$ with the photogenerated $M(CO)_5THF$ intermediate at ambient temperatures. These anionic complexes were also prepared by direct thermal reactions of equimolar amounts of $[Et_4N][M(CO)_5SCPh_3]$ and the hexacarbonyl parent, $M(CO)_6$, in THF solutions. These new complexes were identified by FT-IR, ^{1}H NMR spectroscopies and elemental analyses. Ligand-substitution reactions in these complexes with triethlyl phosphite, $P(OEt)_3$, as an entering ligand in THF solutions resulted in the formation of $[Et_4N][cis\text{-}M(CO)_4(SCPh_3)\{P(OEt)_3\}]$ (M = W, **2a**; Mo, **2b**) as product. A kinetic study of carbon monoxide substitution reactions in these complexes by $P(OEt)_3$ ligand under *pseudo*-first-order reaction conditions indicated that these reactions are first-order in metal substrate and zero-order in $P(OEt)_3$ concentration. The kinetic data for CO substitution reactions support a dissociative mechanistic pathway, which involves initial M-CO bond-breaking followed by fast attack of $P(OEt)_3$ at the resulting coordinatively-unsaturated intermediate. It is evident from the facile CO loss in these anionic complexes that the thiolate ligand, $[SCPh_3]^-$, is acting as a *cis*-CO-labilizing ligand. It is also proposed that the thiolate sulfur atom bound to the metal is acting as a π-donor ligand during CO dissociation, such π–electron donation should result in stabilization of the 16-electron intermediate, $[M(CO)_4SCPh_3]^-$, which is generated during CO dissociation. First-order Rate constants and activation parameters for these CO substitution reactions were determined and are discussed.
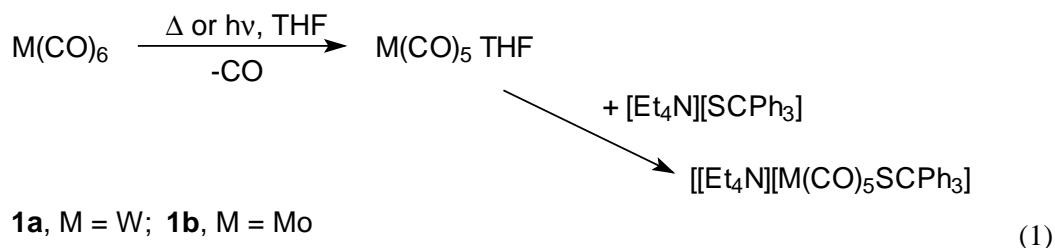
Introduction

The chemistry of organometallic complexes of group 6 metal carbonyls with sulfur-containing ligands in general and studies on the reactivity of Mo-S bond, with molybdenum in low oxidation state, in particular, has received increasing attention over the past two decades. The significance of such studies is mainly due to the occurrence of a Mo-S bond in a number of Mo-containing enzymes.[1,2] Thus, it is important to study the factors that affect the reactivity of M-S bond which will make it possible to tune the electronic and the steric factors around the central metal in complexes which contain these metals in their low or zero oxidation states. In addition, it has been demonstrated that anionic octahedral metal carbonyls of the type $[M(CO)_5X]^-$ are labile complexes and can undergo facile CO substitution reactions under conditions which are rather mild

compared to those complexes which contain only neutral ligands such as complexes of M(CO)$_5$L type (L = phoshine, phosphite, amine).[3,4] A series of these anionic metal carbonyls, [M(CO)$_5$X]$^-$ (X = acetate,[5] formate,[6] carboxylate,[7] thiouracilate,[8] oxalate,[9] phenoxides,[10] silyl,[11] sulfides,[12] and amido[13] ligands) have been reported by Darensbourg and coworkers. The most interesting solution property of these anionic derivatives of group 6 metal carbonyls is their propensity to undergo facile CO dissociation at ambient temperatures. Thus, these X$^-$ anionic ligands have been classified as *cis*-CO labilizing ligands. The *cis*-CO labilizing ability of these anions was explained in terms of ground state destabilization of the complex, and also by transition state stabilization of the resulting coordinatively-unsaturated intermediate,[14] which results upon *cis*-CO dissociation.

We have recently reported the synthesis and the solution reactivity of group 6 pentacarbonyl thiobenzoate anionic complexes. The results of this study indicated that thiobenzoate anion, [SCOPh]$^-$, is a *cis*-CO labilizing ligand.[15] Furthermore, we have illustrated that such type of labilization is mainly electronic in nature. Herein, we report the synthesis and the solution reactivity of a new anionic W(0) and Mo(0) complexes of the type [Et$_4$N][M(CO)$_5$SCPh$_3$].

### Results and discussion

The complexes **1a** and **1b** were synthesized from the reaction of the photogenerated intermediate M(CO)$_5$THF with the thiolate ligand, [Et$_4$N][SCPh$_3$], or directly from the reaction of M(CO)$_6$ with the thiolate ligand in THF solutions as shown in Equation 1,

$$M(CO)_6 \xrightarrow[\text{-CO}]{\Delta \text{ or } h\nu,\ THF} M(CO)_5\ THF$$

$$\xrightarrow{+\ [Et_4N][SCPh_3]} [[Et_4N][M(CO)_5SCPh_3]$$

1a, M = W; **1b**, M = Mo

(1)

The progress of the reaction given in Eq. 1 was monitored by FT-IR spectroscopy, through following the disappearance of the CO stretching frequency, T$_{1u}$, of the hexacarbonyl parent (M = W, at 1974 cm^{-1}, M = Mo at 1981 cm^{-1}). The decay of this

band is a good evidence for the progress of the reaction. It has been observed that the reaction of the anion [SCPh$_3$]$^-$ with M(CO)$_6$ proceed under conditions which are milder than those observed for a dissociative, D, or a dissociative-interchange, I$_d$, mechanisms.[3,4] Thus, it is highly possible that attack of the thiolate anion takes place initially at a carbonyl carbon of M(CO)$_6$ rather than directly at the metal center. This assumption is consistent with the results obtained from molecular orbital calculations on several metal carbonyls which indicated the presence of a residual positive charge on the carbonyl carbon of these complexes which, accordingly, makes this site susceptible to nucleophilic attack, especially if the incoming nuclephile is anionic[16,17] (Scheme 1).
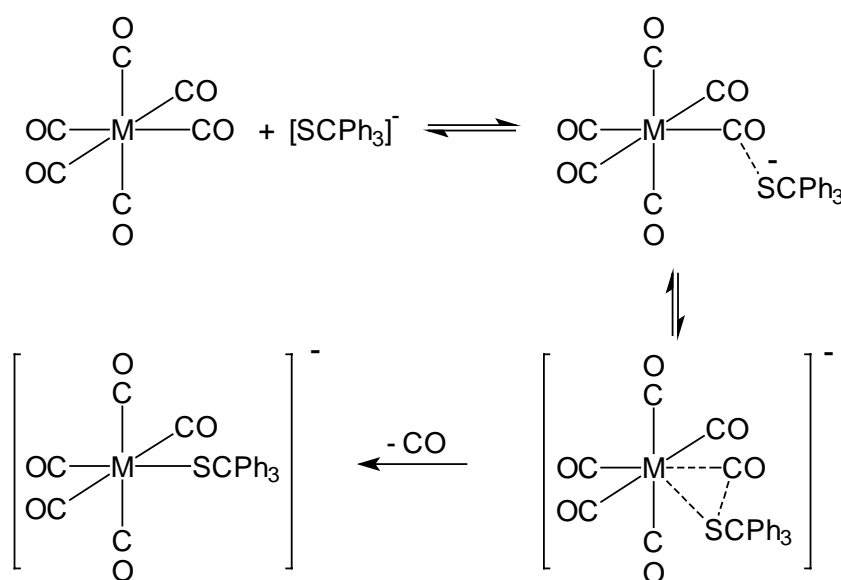

Scheme 1

The complexes **1a** and **1b** are yellow powders, soluble in most polar organic solvent such as THF, CH$_3$CN, and chlorinated hydrocarbons, but insoluble in nonpolar solvents. They are air-stable as solids and in organic solvents, and were characterized by FT-IR, ^{1}H-NMR, and elemental analyses. The IR spectra of these complexes in the carbonyl stretching region exhibited a three-bands pattern corresponding to the terminal CO ligands, which is indicative of the presence of M(CO)$_5$ moiety under *pseudo*-C$_{4v}$ local symmetry. Band assignments were made on the basis of reported frequencies for monosubstituted group 6 metal pentacarbonyls.[18] The ^{1}H NMR spectra of **1a** and **1b**

exhibited signals which are in good agreement with the proposed structure and the chemical shifts for the protons in these complexes appear in the expected region as given in the experimental section *vide infra*.

The complexes **2a** and **2b** are air-stable and soluble in most polar organic solvents. The IR spectra of these complexes in the carbonyl stretching region exhibited a four-bands pattern corresponding to the terminal CO ligands, which is characteristic for the presence of $M(CO)_4$ moiety under *pseudo*-C_{2v} local symmetry
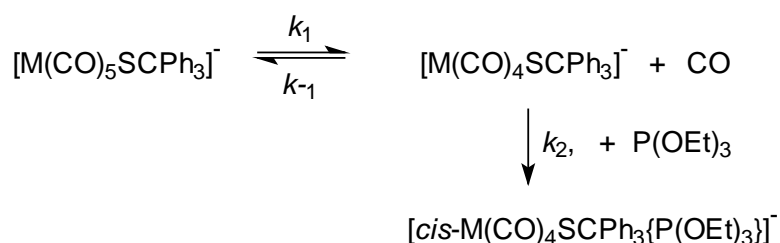
Thermal Kinetics Studies

Carbon monoxide substitution reactions in the complexes **1a** and **1b** with $P(OEt)_3$ as an entering ligand under *pseudo*-first-order reaction conditions in THF solutions proceed according to Equation 2,

$$[Et_4N][M(CO)_5SCPh_3] + L \rightarrow [Et_4N][M(CO)_4(SCPh_3)(L)] + CO \qquad (2)$$

$$L = P(OEt)_3; M = W, Mo$$
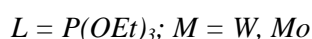
The results of this CO substitution reactions support a rate law, given in equation 3,

$$-\text{Rate} = -dC\{[Et_4N][M(CO)_5SCPh_3]\}/dt = k_{obs} C\{[Et_4N][M(CO)_5SCPh_3]\} \qquad (3)$$

Under pseudo-first-order conditions, the observed rate constants were found to be independent of $P(OEt)_3$ concentrations as shown in Table 1. Thus, a dissociative mechanistic pathway is proposed which involves reversible dissociation of CO from the starting material followed by fast attack of the phosphite ligand at the resulting intermediate as illustrated in Scheme 2.

$$[M(CO)_5SCPh_3]^- \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; [M(CO)_4SCPh_3]^- + CO$$

$$\Big\downarrow k_2, \; + P(OEt)_3$$

$$[cis\text{-}M(CO)_4SCPh_3\{P(OEt)_3\}]^-$$

Scheme 2. All anions are tetraethylammonium salt.

Assuming that $[M(CO)_4SCPh_3]^-$ is a steady state intermediate, k_{obs} is given by,

$$k_{obs} = k_1 k_2 [P(OEt)_3] / (k_{-1}[CO] + k_2 [P(OEt)_3]) \qquad (4)$$

It is expected that under pseudo-first-order conditions $k_2[P(OEt)_3] >> (k_{-1}[CO]$, thus:

$$k_{obs} = k_1 \qquad (5)$$

The observed rate constants at various temperatures and the activation parameters for CO dissociation are given in Table 1. A typical Eyring plot for ligand-substitution reaction in complex 1a is shown in Figure 1. The data suggest that the enthalpies of activation, $\Delta H^{\neq}$, for M-CO bond dissociation (M =W, Mo) closely approximate M-CO Bond dissociation energies in these complexes. These values are in good agreement with those reported for comparable anionic group 6 metal complexes especially those with M-S bond.[8,12,13,15] Entropies of activation, $\Delta S^{\neq}$, for CO dissociation are not highly positive as expected for a dissociative mechanistic pathway. It seems that the facile CO displacement in these complexes is attributed to both steric and electronic effects. The bulky thiolate, $[SCPh_3]^-$, group facilitates the dissociation of a *cis*-CO due to steric factors. In addition, the sulfur atom in this anionic ligand stabilizes the 16-electron intermediate, which is generated during CO dissociation, *via* π-electron donation from the sulfur to the metal center. This observation is in agreement with that proposed by Darensboug and coworkers for the phenoxides,[10] thiouracilate,[8] and aryl sulfides[12] derivatives of group 6 metal carbonyls. It should be mentioned in this regard that π-electron donation, as given in Scheme 3, is reversible and only a partial π-bond, given in dashed line, is formed during the substitutional process, (Scheme 3), which partially compensates for the electronic deficiency on the central metal. This type of bonding occurs concertedly with CO dissociation in these complexes and justifies the small positive values obtained for the entropies of activation, $\Delta S^{\neq}$, during the CO substitutional processes.
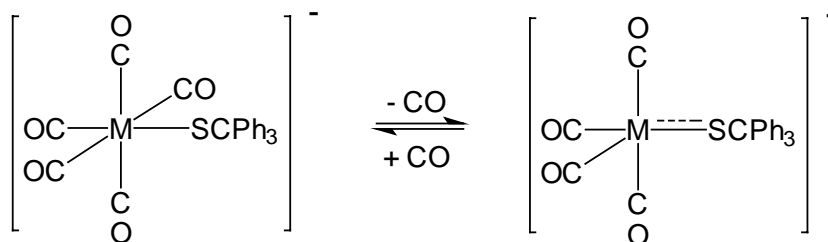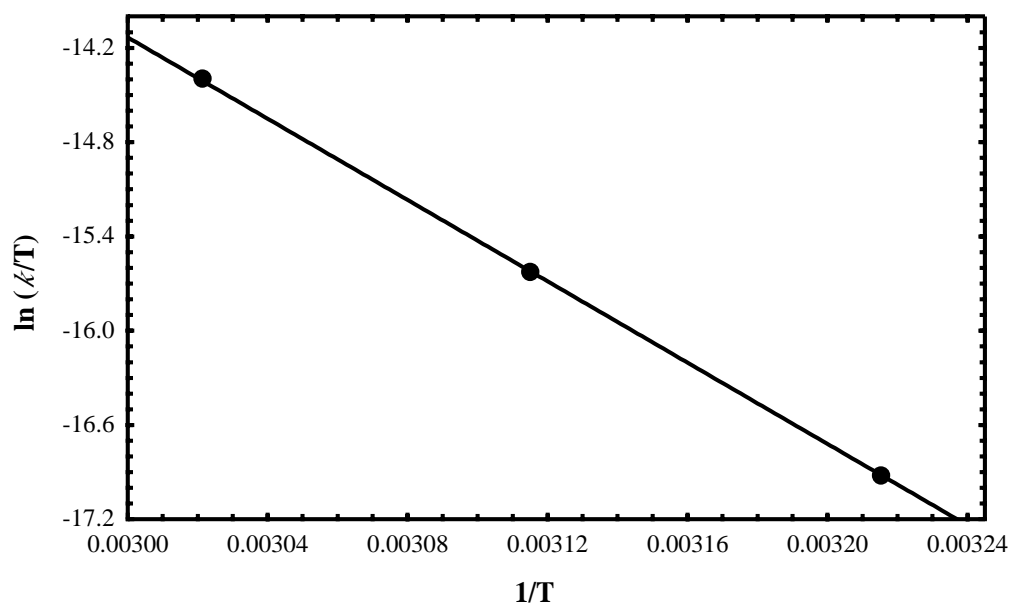

Scheme 3

Figure 1. Eyring plot for CO substitution reaction of **1a** with P(OEt)$_3$ in THF to give **2a**.

Table 1. First-order rate constants at various temperatures and activation parameters for CO substitution reactions in [Et$_4$N][M(CO)$_5$SCPh$_3$] complexes with P(OEt)$_3$ in THF to give [Et$_4$N][*cis*-M(CO)$_4$(SCPh$_3$){P(OEt)$_3$}] products.

M	T, °C	[P(OEt)$_3$], M	10^4 k$_{obs}$, s^{-1}	$\Delta H^{\neq}$, kcal.mol^{-1}	$\Delta S^{\neq}$, (eu)
W	38.0	0.125	1.38(2)	25.7(1)	2.7(3)
		0.222	1.43(6)		
		0.540	1.39(8)		
		0.684	1.40(1)		
	48.0	0.135	5.20(5)		
		0.465	5.18(3)		
		0.828	5.28(9)		
	58.0	0.345	1.78(2)		
		0.460	1.86(6)		
		0.912	1.88(7)		
Mo	20.0	0.125	2.90(3)	25.1(3)	7.4(8)
		0.222	3.15(9)		
		0.480	2.94(6)		
	30.0	0.325	12.2(1)		
		0.650	13.4(8)		
		0.870	12.3(4)		
	40.0	0.238	46.5(7)		
		0.655	45.8(1)		
		0.920	46.3(3)		

Experimental

All reactions were performed under a N_2 atmosphere employing Schlenk techniques.[19] Hexane, THF, and Et_2O were distilled over Na/benzophenone. Absolute methanol and absolute ethanol (Aldrich) were used without further purification. $W(CO)_6$, $Mo(CO)_6$ (Aldrich) and triethyl phosphite (Aldrich) were purified according to literature procedures.[20,21] Et_4NOH (25% w/w in MeOH solution) (Fluka) was used as received.

Photolysis experiments were carried out employing a medium pressure Hg lamp (150 W) with a quartz immersion cell (Heraeus). Infrared spectra were recorded on a Nicolet impact 410 FT-IR spectrophotometer. ^{1}H NMR were recorded using a Bruker, Advance DPX 300 MHz spectrometer with TMS as internal standard. Elemental analyses were performed by the M-H-W laboratories, Phoenix, Arizona, USA.

Synthesis of [Et₄N][SCPh₃]

This salt was prepared by a method similar to that reported in the literature for thiolate salts.[12] Triphenylmetanethiol (2.0 g, 7.24 mmol) was dissolved in 7.0 mL of THF and 10.0 mL of absolute methanol and Et_4NOH (25% w/w in methanol; 4.3 g, 7.3 mmol OH⁻) was added. The mixture was heated under reflux with stirring for ~ 2 h. The reaction mixture was then cooled to room temperature and the volatiles were removed under reduced pressure. The residue was washed three times with 10 mL portions of diethyl ether to give a yellowish solid product. The product was recrystallized from CH_2Cl_2/pentane (1:3 v:v), and was stored under N_2 atmosphere. Yield ~85%. Anal. Calcd for $C_{27}H_{35}NS$: C 79.94, H 8.69, N 3.45. Found: C 79.74, H 8.45, N 3.21.

General Procedure for Synthesis of [Et₄N][M(CO)₅SCPh₃] (M = W, Mo)

A THF solution (150 mL) of $M(CO)_6$ (0.71 mmol) was irradiated with UV light under N_2 stream at room temperature for 2 h to generate the $M(CO)_5THF$ intermediate. To this solution [Et₄N][SCPh₃] (0.67 mmol) was added and the mixture was stirred for about one hour at room temperature. The solution was filtered through *Celite* and the solvent was removed under reduced pressure. Orange crystals were isolated upon addition of 30 mL of Et_2O/hexane mixture (1:2 v:v) at ~ -15 °C.

These complexes were also prepared thermally from the hexacarbonyl parent by reacting $M(CO)_6$ (0.57 mmol) and $[Et_4N][SCPh_3]$ (0.51 mmol) in THF solution (30 mL) under a N_2 atmosphere under reflux for 2 h. The product was obtained by the same work-up procedure as before.

$[Et_4N][W(CO)_5SCPh_3]$ (1a): Yield ~80%. IR (THF) ν_{CO} 2051w, 1911vs, 1856 m cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ 1.16 (t, 12H, 4CH$_3$), 3.21 (q, 8H, 4CH$_2$), 7.13-7.48 (m, 15H, 3ArH). Anal. Calcd for $C_{32}H_{35}O_5NSW$: C 52.68, H 4.84, N 1.92. Found: C 52.58, H 5.47, N 2.05.

$[Et_4N][Mo(CO)_5SCPh_3]$ (1b): Yield ~65%. IR (THF) ν_{CO} 2053w, 1919vs, 1860m cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ 1.16 (t, 12H, 4CH$_3$), 3.21 (q, 8H, 4CH$_2$), 7.05-7.13 (m, 15H, 3ArH). Anal. Calcd for $C_{32}H_{35}O_5NSMo$: C 59.90, H 5.50, N 2.19. Found: C 59.45, H 5.34, N 2.08.

General Procedure for Synthesis of $[Et_4N][cis\text{-}M(CO)_4(SCPh_3)\{P(OEt)_3\}]$

$[Et_4N][M(CO)_5SCPh_3]$ (0.22 mmol) and four-fold excess of $P(OEt)_3$ (0.88 mmol) were allowed to react in THF solution under a N_2 atmosphere (M = W, T = 50 °C; M = Mo, T = 40 °C) for about two hours. The solution was cooled to room temperature and filtered through *Celite*. The solvent was removed under reduced pressure to give a bright yellow solid product which collected by suction filtration and recrystallized from THF/hexane mixture (1:5 v:v) at ~ -20 °C.

$[Et_4N][cis\text{-}W(CO)_4(SCPh_3)\{P(OEt)_3\}]$ (2a): Yield ~75%. IR (THF) ν_{CO} 2055m, 1882s, 1874vs, 1817s cm^{-1}. Anal. Calcd for $C_{37}H_{50}NO_7PSW$: C 51.22, H 5.81, N 1.61. Found: C 50.89, H 5.64, N 1.52.

$[Et_4N][cis\text{-}Mo(CO)_4(SCPh_3)\{P(OEt)_3\}]$ (2b): Yield ~70%. IR (THF) ν_{CO} 2061m, 1890s, 1881vs, 1823s cm^{-1}. Anal. Calcd for $C_{37}H_{50}O_7NPSMo$: C 56.99, H 6.46, N 1.80. Found: C 57.55, H 6.25, N 1.95.

Determination of Reaction Rates

Ligand-Exchange reactions in the complexes $[Et_4N][M(CO)_5SCPh_3]$ (M = W, Mo) with triethyl phosphite, $P(OEt)_3$, in THF solutions were followed by FT-IR spectroscopy through monitoring the gradual disappearance of the carbonyl stretching frequency A_1 at 2051 cm^{-1} for M = W and 2053 cm^{-1} for M = Mo. Base-line correction

of the IR spectra were performed as described elsewhere.[15,22] Initial substrate concentrations of about 4×10^{-4} M were employed, and pseudo-first order reaction conditions were maintained through use of at least thirty-fold excess of the entering nucleophile P(OE)$_3$ in THF solutions. Samples were periodically withdrawn from the solution and examined by FT-IR spectroscopy. Plots of ln ($A_t - A_\infty$) versus time (A_t and A_∞ being the absorbance at time = t and at t > five half-lives, respectively) were linear to at least four half-lives, and gave slopes which are the pseudo-first-order rate constants, $k_{obs,}$ for the reactions. Rate data were analyzed employing a linear-least-squares fitting program. Activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were determined from the Eyring plots, by plotting ln (k/T) versus 1/T as shown in Fig. 1. Rate constants and activation parameters are given in Table I. Limits of error, are given in parentheses as the uncertainties of the last digit(s) of the experimental values, are one standard deviation.

Acknowledgments

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Povzetek

Komplekse [Et$_4$N][M(CO)$_5$SCPh$_3$] (M = W, **1a**; Mo, **1b**) smo pripravili z reakcijo med [Et$_4$N][SCPh$_3$] in in fotolitsko dobljenim M(CO)$_5$THF in tudi z reakcijo med [Et$_4$N][M(CO)$_5$SCPh$_3$] in M(CO)$_6$. Z zamenjavo karbonilnih ligandov s P(OEt)$_3$smo pripravili [Et$_4$N][cis-M(CO)$_4$(SCPh$_3$){P(OEt)$_3$}] (M = W, **2a**; M = Mo = **2b**). Reakcija je psevdoprvega reda na koncentracijo kompleksa in ničelnega reda na koncentracijo P(OEt)$_3$. Kinetika reakcije kaže na disociacijski mehanizem zamenjave ligandov, v katerem tiolatni ligand, [SCPh$_3$]$^-$ destabilizira cis-CO ligand in stabilizira 16-elektronki disociacijski intermediat [M(CO)$_4$SCPh$_3$]$^-$. Za reakcijo substitucije smo določili reakcijske konstante in aktivacijske parametre.