

Disconnection of the organic moiety in chromium and tungsten complexes [(dithiin)M(CO)₅]

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ABSTRACT: The reaction of 5-alkylthio-3*H*-1,2-dithiole-3-thione derivatives with Fischer alkoxy carbenes gives 1,3-dithiin dithioorthoesters derivatives complexed with M(CO)₅ (M = Cr or W). We report here that the dithiin derivative free of metal can be obtained by ligand exchange using acetonitrile, methanol, phenyl methyl sulfide or (Ph)₃P. Methanol gives the best results from a preparative point of view. The reaction with acetonitrile was shown to be reversible and the kinetic of ligand exchange and the activation parameters were determined. From these data it is concluded that the mechanism is predominantly dissociative for M = Cr and it has some contribution of the associative mechanism for M = W. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: Dithiin complexes; ligand exchange; dithioorthoesters; chromium; tungsten

INTRODUCTION

We recently reported that the reaction of Fischer carbenes with 5-alkylthio-3*H*-1,2-dithiole-3-thione derivatives leads to the insertion of the carbene into the five-member ring yielding complexes of type **1**.¹ The products obtained in those reactions belong to a novel type of 1,3-dithiin dithioorthoesters that fill a large gap in the synthetic methodology for the preparation of the scarcely known 1,3-dithiin derivatives,² or the extremely rare compounds having a dithioorthoester group.³ The *in vitro* cytotoxicity toward cancer cell lines of 2-vinyl-4*H*-1,3-dithiin from extracts of *Allium victorialis* has been reported⁴ (Chart 1).

We considered of interest to find an easy way to disconnect the metal from the complex **1** in order to get the organic compound free of metal **2**. In the literature there are examples of thiocarbonyl derivatives complexed with M(CO)₅ (M = Cr or W) where the metal is coordinated with the thiocarbonyl group but the metal could not be disconnected without decomposing the organic skeleton.⁵ On the other hand, there are a few examples of complexes with Mn where one of the ligands is an organic sulfide which, under appropriate conditions, can be exchanged with other ligand of

the same or similar nature through a dissociative mechanism.⁶

In the complexes **1a–c** the metal may be coordinated to the double bond, the exocyclic sulfur, the thiocarbonyl group or the sulfur atoms of the ring. Spectroscopic evidences pointed to the coordination to the carbon–carbon double bond (η^2).¹ Reactions of exchange of

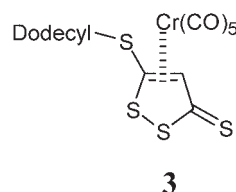
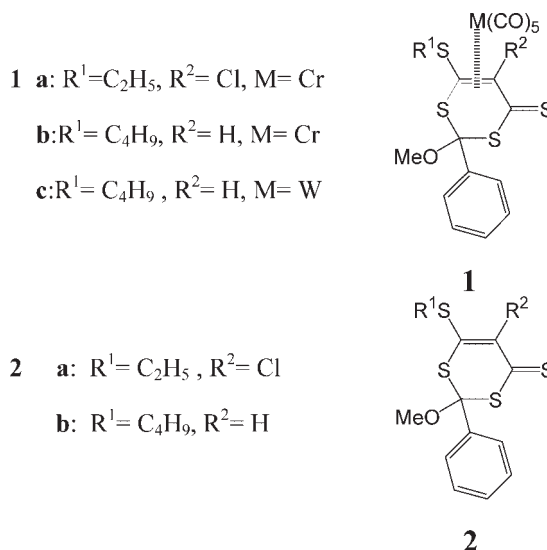


Chart 1.

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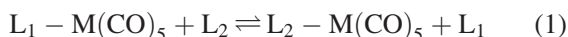
ligands at the metal atom are of interest because of the significance of transition-metal chemistry to modern synthesis and catalysis.⁷

In this paper we report the efficiency of several compounds to displace the ring from the coordination sphere of the metal. Besides we also present here a kinetic study of the displacement of the 1,3-dithiin ring of **1a–c** by acetonitrile from which it is concluded that for some of the complexes the exchange of ligands involves mainly a dissociative mechanism, whereas with others there is significant contribution of the associative mechanism depending on which metal is in the complex. It is important to note that to the best of our knowledge, there are no antecedents in the literature regarding kinetic studies of ligand-exchange reactions in stable complexes of type $L(\text{CO})_5\text{M}$.

RESULTS AND DISCUSSION

There are several examples in the literature which show that complexes of type $L(\text{CO})_3\text{M}$ with $\text{M} = \text{Cr}$ or W and $L = \text{organic ligand}$ are demetalated under very mild conditions such as irradiation with sunlight and air oxidation at room temperature.^{8,9} These conditions were not appropriate to demetalate complexes **1a–c** on a preparative scale because under long irradiation time under air only unreacted material and decomposition products were isolated. We did not consider the use of pyridine oxide,¹⁰ dimethyldioxirane,¹¹ or dimethylsulfoxide to demetalate the complexes because in these reactions the oxidized ligand is obtained therefore the expected products for the reactions of **1a–c** with these reagents would not be **2a–b** but oxidized derivatives.

In order to eliminate the metal from complex **1a–c** we use ligands that could compete with the 1,3-dithiin ring for the metal coordination (Equation 1)



As competing ligands we used acetonitrile (ACN), hydrogen sulfide (H_2S), methyl phenyl sulfide (PhSMe), triphenyl phosphine (Ph_3P), and methanol (MeOH).¹² The results are summarized on Table 1. It can be seen that except for H_2S all the other ligands displaced the 1,3-dithiin ring **2a–b** from **1a–c**, but MeOH is the one that gave the best results. The products were characterized using ^1H and ^{13}C NMR and HRMS. The main ^{13}C NMR spectral differences between **1a–c** and **2a–b** are: (a) the signals corresponding to the $\text{C}=\text{O}$ of $\text{M}(\text{CO})_5$ are not present in **2a–b**, the signal corresponding to the ring carbons six and five are shifted 2.6 and 0.8 ppm downfield, respectively, (b) the signal corresponding to the carbon of the thiocarbonyl is shifted 2.2 ppm downfield, and (c) all the other signals are shifted 0.2–0.8 ppm downfield. In the ^1H NMR the main difference is

Table 1. Disconnection of the $\text{M}(\text{CO})_5$ moiety under preparative conditions

L	% 2a ^a	% 2b ^a
ACN ^b	37.7	58 ^c
Ph-S-Me ^d	50	40
$\text{P}(\text{Ph})_3$ ^e	18.4	17.6
MeOH ^f	54	78
H_2S ^g	Unreactive	Unreactive

^a Obtained from **1a** and **1b**, respectively.

^b 0.11 mmol of complex were dissolved in 30 mL acetonitrile at 80 °C, reaction time 30 min.

^c The yield increased from 25 to 58% when air was bubbled through the solution instead of N_2 .

^d 0.11 mmol of complex and 1.1 mmol of Ph-S-Me in boiling methylene chloride. Reaction time 20 h.

^e 0.11 mmol of complex and 1.1 mmol of Ph_3P in dioxane at 60 °C, reaction time 3 h.

^f 0.11 mmol of complex dissolved in 30 mL of methyl alcohol at 70 °C with air pumped, reaction time 6 h.

^g SH_2 produced from the reaction of $[\text{HCl}]$ and FeS in a separate flask was bubbled through a solution of 0.11 mmol of complex in methylene chloride at room temperature during 3 h.

seen in the ring proton which appears 0.21 ppm upfield in **2a–b** compared with **1a–c**, all the other signals change only 0.05–0.1 ppm. The agreement between the HRMS experiments and the molecular weight calculated, together with the NMR experiments, allows the confirmation of structures **2a–b** free of metal and without modifications of the organic skeleton.

Using acetonitrile to disconnect the metallic moiety in compounds **1a–c**, we found that the complexes could be re-generated after the displacement. This was done evaporating the solvent to dryness, and then adding other solvent, such as methylene chloride or hexane. Under this conditions complexes **1a–b** were formed without detectable by-products indicating that with acetonitrile as competing ligand the reaction is reversible.

In order to get more insight into the mechanism of the displacement of the 1,3-dithiin ring we determined the rate constant for the reactions of **1a** in acetonitrile, 1,4-dioxane, MeOH, and hexane at 45 °C. In all solvents, except for hexane, the maximum absorption at 578–627 nm decreases strongly whereas the maximum at 375–405 nm shift to 377–412 nm, and slightly increases in intensity (Fig. 1 is representative). In hexane the behavior is quite different as shown in Fig. 2. The spectrum shows a decrease in the absorbance with time in all range of wavelengths studied. Similar behavior was observed with complexes **1b–c** in hexane. We attribute these differences to the fact that hexane is a very weak coordinating agent for $\text{Cr}(\text{CO})_5$ so this species decompose in the reaction solution. The values of the observed pseudo-first-order rate constant for disconnection of the metallic moiety in the different solvents are shown in Table 2.

The fact that a very well-defined isosbestic point is observed (Fig. 1 is representative) indicate that compounds **1a–c** are transformed into compounds **2a–b**

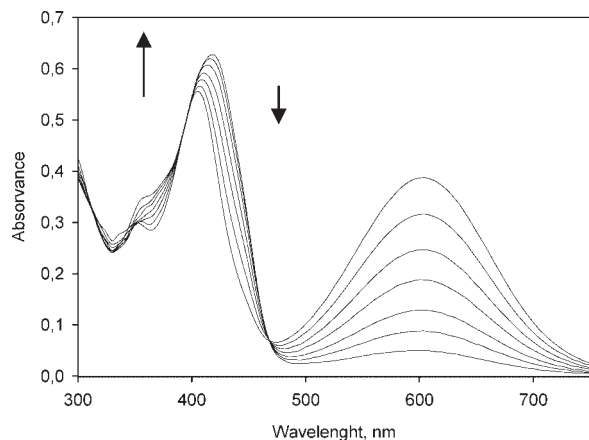


Figure 1. Spectral changes as a function of time for the reaction of **1b** in acetonitrile at 45°C. $[1b] = 5 \times 10^{-5}$ M. Time elapsed 2 h.

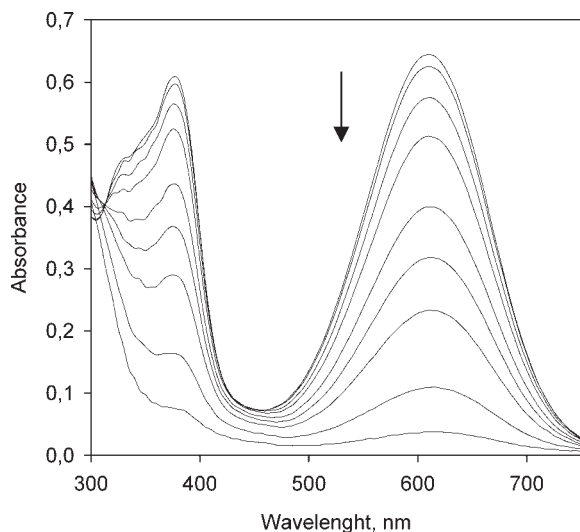


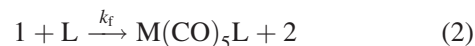
Figure 2. Spectral changes as a function of time for complex **1b** in hexane at 45°C. Time elapsed 4 h.

Table 2. Observed rate constants for 1,3-dithiin displacement reactions in complex **1b** at 45°C

Solvent (λ , nm) ^a	k_{obs} , 10^{-4} s ⁻¹
Acetonitrile (583)	21.2 ± 0.01
Hexane (609)	0.88 ± 0.01
1,4-Dioxane (627)	11.38 ± 0.01
Methyl alcohol (578)	9.05 ± 0.06

^a Values within bracket are the wavelength used for the rate constant determinations.

(Eqn (2)) in a clean reaction, without accumulation of any intermediate



We attempted the determination of the rate constant for the reverse reaction of Eqn (2) ($L = \text{acetonitrile}$) and so after the reaction with **1a** ended we added up to 2.5 M **2a** but we could not see any reversion to the substrate **1a**. Considering that we could detect 5% formation of **1a**, we can estimate that the second order rate constant for the reaction of **2a** with $\text{Cr}(\text{CO})_5$ (acetonitrile) is lower than $0.4 k_f$.

The ligand exchange reaction was also carried out at different temperatures in order to determine the activation parameters of the reaction. The values of the pseudo-first-order rate constant for the disconnection of the metallic moiety of several complexes in acetonitrile are shown in Table 3, together with the data corresponding to complex **3** for comparison. The data of activation parameters are summarized in Table 4.

There are several reports in the literature which demonstrate that it is possible to generate intermediates coordinatively unsaturated such as $\text{Cr}(\text{CO})_5$ from the photochemical rupture of a $\text{Cr}-\text{CO}$ coordination bond. This intermediate rapidly reacts with the solvent to form $[(\text{solvent})\text{Cr}(\text{CO})_5]$ where the solvent occupies the internal coordination sphere of $\text{Cr}(\text{CO})_5$ and forms a coordination bond with the metallic center.¹³ These studies have been of great importance to get insight into the process of solvation of metallic intermediates. This is crucial to determine the catalytic selectivity since the solvent is replaced by the reactive substrate. Much less is

Table 3. Effect of temperature on the observed rate constant for ligand exchange in complexes **1a–c** and **3** in acetonitrile

Temperature °C ^a	1a^b	1b^b	1c^b	3^b
	k_{obs} , 10^{-4} s ⁻¹			
15	0.413 ± 0.003			
25	1.69 ± 0.02	0.824 ± 0.003		1.43 ± 0.01
35	6.69 ± 0.03	3.22 ± 0.04	0.425 ± 0.005	5.13 ± 0.03
45	21.2 ± 0.01	10.2 ± 0.01	1.084 ± 0.005	16.35 ± 0.05
55			3.69 ± 0.04	

^a The temperature was controlled within ± 0.1 °C.

^b The concentration of complexes into the cell was 5×10^{-5} M, the errors are standard deviations of the fit in the Absorbance versus time data.

Table 4. Activation parameters for the acetonitrile reaction with **1a–c** and **3**

	1a ^a	1b ^b	1c ^c	3 ^b
E_a , Kcal mol ⁻¹	25.4	25.0	21.3	22.9
ΔH^\ddagger , Kcal mol ^{-1d}	24.7	24.7	20.7	22.3
ΔS^\ddagger , e.u.	7.73	4.48	-12.0	-1.26

^a Temperature range 15–45 °C.^b Temperature range 25–45 °C.^c Temperature range 35–55 °C.^d Calculated as $\Delta H^\ddagger = E_a - RT$ at 45 °C.Calculated from $\Delta S^\ddagger = (\log k - 10.753 - \log T + E_a/4.576 T) \times 4.576$ at 45 °C.

known about the displacement of other compounds from the metallic center. We think that the understanding of this process could be important for the determination of the mechanism of reaction mediated by metal complexes.

According to the rule of the 18 electrons,¹⁴ we can consider complex **1** as saturated coordinatively. The known mechanisms in the displacement of ligands such as pyridine or THF are: dissociative (mechanism D) and associative (mechanism A). It has been suggested that the predominance of any of these mechanisms depends on the metallic center and the steric requirements of the incoming and leaving ligands.^{15,16}

Considering the two possible mechanisms for the exchange reaction we suggest for Eqn (2), the general mechanism shown in Scheme 1 where the dissociative (formation of intermediate $M(CO)_5$) and associative ($k_3[L]$ step) mechanisms are considered.

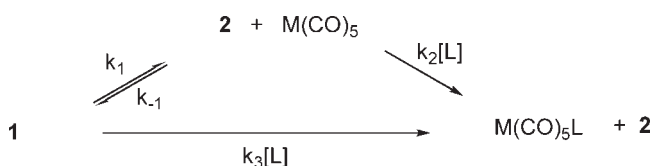
Considering $M(CO)_5$ as a steady state intermediate, the observed rate constant is given by Eqn (3).

$$k_{\text{obs}} = \frac{k_1 k_2 [L]}{k_{-1} [2] + k_2 [L]} + k_3 [L] \quad (3)$$

From photoacoustic calorimetry it was determined that the second order rate constants for the reaction of $Cr(CO)_5$ with acetonitrile, tetrahydrofuran, methanol and 1-hexene are in the range of 10^7 – $10^8 M^{-1} s^{-1}$, so the value expected for k_{-1} and k_2 must be in this range. The concentration of **2** is much smaller than that of L since the latter is the solvent and therefore the condition $k_{-1}[2] \ll k_2[L]$ holds and Eqn (3) can be simplified to Eqn (4).

$$k_{\text{obs}} = k_1 + k_3 [L] \quad (4)$$

The fact that the values of activation entropy for the disconnection in complexes **1a** and **1b** are positive,



suggest that the dissociative mechanism is predominant, although this is not conclusive evidence.¹⁶ The ideal way to determine the contribution of each of the terms of Eqn (4) is to run an experiment where the concentration of L is changed, however in this case is not possible because L is the solvent.

For the complex **1c** with $W(CO)_5$, the activation entropy is negative and this result is consistent with literature reports which indicate that for ligands such as pyridine and phosphines the associative mechanism becomes more important as the metallic group increases in size, as is evident in the series Cr, Mo, W.¹⁶

Comparing the activation entropy of **1b** and **1c** we conclude that the metal is very important to determine the predominant mechanism. On the other hand, comparison of the value for **3** with those of **1a** and **1b**, that have the same metal, shows that the ligand is also important, and is evident that a bigger steric hindrance in the coordination site in the leaving ligand, leads to a more dissociative mechanism.

CONCLUSIONS

We could effectively disconnect the metallic moiety from complexes of type **1** with $M(CO)_5$ by ligand exchange using several compounds. Methyl alcohol is the best reagent from a preparative point of view. With acetonitrile the displacement was complete but the yield is lower than that with methyl alcohol because the reaction is reversible and some product is lost in the form of complex **1** during work-up. With the other ligands, the yield decreases because of the formation of by-products during the reaction. From the kinetic data and the corresponding activation parameters for the disconnection with acetonitrile, we conclude that a dissociative mechanism is predominant for the transference of ligands when chromium is the metallic center of the complexes, whereas when tungsten is the metallic center there is some contribution of the associative mechanism. To the best of our knowledge this reaction represents the first report of rate constant for ligand exchange in stable complexes of type $L(CO)_5M$.

EXPERIMENTAL SECTION

Nuclear magnetic resonance (¹H and ¹³C) spectra were recorded on a Bruker AC 200 (200 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference, spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on a Nicolet FT-IR Avatar 360 spectrometer. Band positions are reported in reciprocal centimeters (cm^{-1}).

Molecular weights were determined from high resolution FAB mass spectra done on a nitrobenzyl matrix (NBA) on a VG-ZAB spectrometer. The spectra were recorded in the UCR Mass Spectrometry Laboratory, Riverside, California. Elemental analysis was carried out by Galbraith Laboratories, Knoxville, TN.

The compounds were purified by column chromatography using silica gel 60 Merck (0.063–0.2 mm) and hexane/CH₂Cl₂ 70/30 v/v as eluent.

Dioxane was distilled from sodium and stored on sodium wires. CH₂Cl₂ and hexane were analytical grade and used as received. All commercially available reagents were obtained in reagent grade and used without purification.

Disconnection with methyl alcohol

A solution of 0.11 mmol of complex **1** in 30 mL of methyl alcohol was heated at 70 °C with a continue bubbling of air. The reaction takes place also under normal atmosphere but the air bubbling facilitates the *work-up*. After 6 h the solution color changes from deep blue to brown-red. The evolution of the reaction was followed by TLC and the reaction was stopped when all the substrate disappears. The solution was filtered and the solvent was removed at low pressure. Then the mixture was purified by column chromatography on silica gel using a mixture of hexane and methylene chloride as elution solvent. The heterocycles **2a–c** so obtained were characterized and stored in dark recipients.

Characterization of the products

6-butylthio-4-methoxy-4-phenyl-4H-1,2-dithiin-3-thione 2a. HRMS (nitrobenzyl alcohol): calculated for C₁₅H₁₈S₄O: 343.0318; obtained 343.0319; ¹³C RMN (50 MHz, DCCl₃), δ ppm: 13.51; 21.87; 30.60; 33.48; 54.19; 97.38; 127.39; 128.39; 128.88; 130.05; 136.19; 151.37; 208.09. ¹H RMN (200 MHz, DCCl₃) δ ppm: 0.96 (t, 6.94 Hz, 3H); 1.47 (m, 2H); 1.71 (m, 2H); 3.09 (m, 2H); 3.34 (s, 3H); 7.48 (s, 1H); 7.43–7.71 (m, 5H). IR cm⁻¹ (KBr): 751.7; 865.8; 893.3; 944.5; 1042.8; 1094.1; 1216.0; 1448.1; 1491.4; 1629.1; 1739.3; 1715.7; 2337.4; 2364.9; 2852.8; 2923.7; 2963.0.

5-Chloro-6-ethylthio-4-methoxy-4-phenyl-4H-1,2-dithiin-3-thione 2b. HRMS (nitrobenzyl alcohol): calculated for C₁₃H₁₃S₄OCl: 347.9539; obtained: 347.9540. ¹³C RMN (50 MHz, (CD₃)₂CO), δ ppm: 12.41; 30.74; 54.30; 96.63; 117.82; 126.14; 128.49; 129.33; 140.45; 148.04; 209.86. ¹H RMN (200 MHz, (CD₃)₂CO) δ ppm: 1.37 (t, 7.3 Hz, 3H); 3.15 (c, 7.3 Hz, 2H); 4.03 (s, 3H); 7.37–7.89 (m, 6H). IR cm⁻¹(KBr): 653.3; 704.5; 838.2; 897.3; 972.0; 1015.3; 1105.8;

1184.5; 1235.7; 1282.9; 1452.1; 1507.2; 1731.4; 2337.4; 2361.0; 2919.7; 2951.1.

pentacarbonyl (5-dodecylthio-3H-1,2-dithiol-3-thione) chromium 3. 0.1 mmol of 5-dodecylthio-3H-1,2-dithiol-3-thione, 0.3 mmol of Cr(CO)₆ and 10 mL of benzene were added to a quartz tube. The mixture was irradiated at 237.5 nm with a 6 W lamp during 1 h. Then the solvent was evaporated and the crude was filtered through silica gel. The complex **3** was obtained pure, yield 80%. (C₂₀H₂₆S₄O₅Cr); ¹³C RMN (50 MHz, CDCl₃), δ ppm: 14.03; 22.63; 28.55; 28.87; 29.32; 29.52; 31.85; 36.25; 133.66; 173.02; 213.33; 215.02; 222.68.

Kinetic determinations. For all complexes in different solvents the same procedure was followed:

A solution of the complex in the solvent used for the kinetic study with an appropriate concentration (~1 mg mL⁻¹) was prepared in a flask which was protected from light and stored at -8 °C until its utilization. The reaction was initiated adding a few microliters of this solution to 3 mL of the solvent contained in a quartz cell placed in the cell compartment of the UV-2101PC Shimadzu spectrophotometer at constant temperature. The final concentration of the complex was 5 × 10⁻⁵ M. The spectral changes were recorded at various time intervals and then the absorbance versus time change at a selected wavelength (Table 2) was used to calculate the rate constant. In all cases clean pseudo-first-order behavior was observed.

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