

# Syntheses, X-ray structures, and reactions of ruthenium carbonyl complexes containing 1,1-dithiolates

Kom-Bei Shiu <sup>a,\*</sup>, Shin-Jay Yu <sup>a</sup>, Yu Wang <sup>b</sup>, Gene-Hsiang Lee <sup>b</sup>

<sup>a</sup> Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan, ROC

<sup>b</sup> Instrument Center, National Taiwan University, Taipei 106, Taiwan, ROC

Received 27 September 2001; received in revised form 15 November 2001; accepted 26 November 2001

## Abstract

Treatment of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  or  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$  with uni-negative 1,1-dithiolate anions via potassium dimethyldithiocarbamate, sodium diethyldithiocarbamate, potassium *tert*-butylthioxanthate, and ammonium *O,O'*-diethylthiophosphate gives both monomeric and dimeric products of *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}(\text{SS}))_2]$  ( $(\text{SS})^- = \text{Me}_2\text{NCS}_2^-$  (**1**),  $\text{Et}_2\text{NCS}_2^-$  (**2**),  $\text{tBuSCS}_2^-$  (**3**),  $(\text{EtO})_2\text{PS}_2^-$  (**4**)) and  $[\text{Ru}(\text{CO})(\eta^2\text{-}(\text{Me}_2\text{NCS}_2))(\mu, \eta^2\text{-}\text{Me}_2\text{NCS}_2)]_2$  (**5**). The lightly stabilized MeCN ligands of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  are replaced more readily than the bound acetate ligands of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$  by thiolates to produce *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}(\text{SS}))_2]$  with less selectivity. Structures **1** and **5** were determined by X-ray crystallography. Although the two chelating dithiolates are *cis* to each other in **1**, the dithiolates are *trans* to each other in each of the  $\{\text{Ru}(\text{CO})(\eta^2\text{-}\text{Me}_2\text{NCS}_2)\}$  fragment of **5**. The dimeric product **5** can be prepared alternatively from the decarbonylation reaction of **1** with a suitable amount of  $\text{Me}_3\text{NO}$  in MeCN. However, the dimer  $[\text{Ru}(\text{CO})(\eta^2\text{-}\text{Et}_2\text{NCS}_2)(\mu, \eta^2\text{-}\text{Et}_2\text{NCS}_2)]_2$  (**6**), prepared from the reaction of **2** with  $\text{Me}_3\text{NO}$ , has a structure different from **5**. The spectral data of **6** probably indicate that the two chelating dithiolates are *cis* to each other in one  $\{\text{Ru}(\text{CO})(\eta^2\text{-}\text{Et}_2\text{NCS}_2)\}$  fragment but *trans* in the other. Both **5** and **6** react readily at ambient temperature with benzyl isocyanide to yield *cis*- $[\text{Ru}(\text{CO})(\text{CNCH}_2\text{Ph})(\eta^2\text{-}(\text{SS}))_2]$  ( $(\text{SS}) = \text{Me}_2\text{NCS}_2^-$  (**7**) and  $\text{Et}_2\text{NCS}_2^-$  (**8**)). A dimerization pathway for *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}(\text{SS}))_2]$  via decarbonylation and isomerization is proposed. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Ruthenium; Carbonyl; Dithiocarbamate; Thioxanthate; Dithiophosphate; Alkyl isocyanide

## 1. Introduction

In the course of a program of synthesis and structural characterization of a series of 1,1-dithiolate complexes of the type *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}(\text{SS}))_2]$  ( $(\text{SS})^- = \text{Me}_2\text{NCS}_2^-$  (**1**),  $\text{Et}_2\text{NCS}_2^-$  (**2**),  $\text{tBuSCS}_2^-$  (**3**),  $(\text{EtO})_2\text{PS}_2^-$  (**4**)), following a similar procedure reported for *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}\text{S}_2\text{PMe}_2)_2]$  from  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$  [1], we have obtained on one occasion small amount of another product (**5**), either from  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$  or a derived complex with lightly stabilized ligands MeCN,  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  [2]. The elemental analysis results of **5** appear consistent with the formulation of  $[\text{Ru}(\text{CO})(\eta^2\text{-}$

$(\text{Me}_2\text{NCS}_2))(\mu, \eta^2\text{-}\text{Me}_2\text{NCS}_2)] \cdot 1/2\text{CH}_2\text{Cl}_2$ , but the real structure cannot be assigned without any ambiguity. It may be a mononuclear product with a half  $\text{CH}_2\text{Cl}_2$  molecule as one chloro ligand around Ru [3], or a dinuclear product, as a  $\text{CH}_2\text{Cl}_2$  solvate, through sulfur coordination in a chelating–bridging mode [4]. If it is a dimeric compound, the related structure may adopt one of the three possible configurations: configuration **A** contains two *cis*-disposed dithiolates; configuration **B** contains two *trans*-disposed dithiolates; and configuration **C** contains one *cis*- and one *trans*-dithiolates around each metal atom (Chart 1).

We report here the results of an X-ray study of **5** which definitely settles the question of its solid-state structure to be dimeric with configuration **B**. This work, along with the results of an X-ray study of **1** and a reactivity study of **1** and **2**, has revealed the dimerization pathway for *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}(\text{SS}))_2]$  via decarbonylation and isomerization.

\* Corresponding author. Fax: + 886-6-274-0552.

E-mail address: kbshiu@mail.ncku.edu.tw (K.-B. Shiu).

## 2. Experimental

The compounds  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  [2a] and  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$  [5] were prepared according to literature methods. All the reactions were performed under prepurified nitrogen using freshly distilled solvents.  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR spectra were recorded in a Bruker AMC400 spectrometer ( $^1\text{H}$ , 400 MHz;  $^{31}\text{P}$ , 162 MHz) calibrated against internal deuterated solvents ( $^1\text{H}$ ) or external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). IR spectra were recorded in a Bio-Rad FTS 175 instrument. Microanalyses were carried out by the staff of the Micro-analytical Service of the Department of Chemistry, National Cheng Kung University.

### 2.1. Preparation of *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-Me}_2\text{NCS}_2)_2]$ (1) and $[\text{Ru}(\text{CO})(\eta^2\text{-Me}_2\text{NCS}_2)(\mu, \eta^2\text{-Me}_2\text{NCS}_2)_2]$ (5)

#### 2.1.1. Method A

Potassium dimethyldithiocarbamate monohydrate (0.830 g, 4.68 mmol) was added directly to a stirred yellow solution of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$ , prepared in situ from *catena*- $[\text{Ru}(\text{CO})_2(\mu, \eta^2\text{-O}_2\text{CMe})]$  (0.190 g, 0.88 mmol), in 36 ml of THF. The color changed immediately to orange–brown. The mixture was stirred for 3.5 h and then taken to dryness under vacuum. Recrystallization using  $\text{Et}_2\text{O}$ – $\text{MeOH}$  from this solid residue gave 0.244 g pale-yellow *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-Me}_2\text{NCS}_2)_2]$  (1) (yield 70%). Then, recrystallization using  $\text{CH}_2\text{Cl}_2$ –hexane from the remaining solid gave orange–brown  $[\text{Ru}(\text{CO})(\eta^2\text{-Me}_2\text{NCS}_2)(\mu, \eta^2\text{-Me}_2\text{NCS}_2)_2\text{-CH}_2\text{Cl}_2]$  (5) (31 mg, 9%). 1, Anal. Calc. for  $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_2\text{RuS}_4$ : C, 24.17; H, 3.04; N, 7.05. Found: C, 23.88; H, 3.05; N, 7.03%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  3.26 (s, 6H, Me), 3.28 (s, 6H, Me). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  2039 (s), 1972 (s). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  2024 (s), 1962 (s). 5, Anal. Calc. for  $\text{C}_{14}\text{H}_{24}\text{N}_4\text{O}_2\text{Ru}_2\text{S}_8\text{CH}_2\text{Cl}_2$ : C, 21.87; H, 3.18; N, 6.80. Found: C, 21.67; H, 3.19; N, 6.78%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  3.22 (br, 6H, Me), 3.36 (br, 6H, Me), 3.60 (br, 6H, Me), 3.62 (br, 6H, Me), 5.32 (s, 2H,  $\text{CH}_2\text{Cl}_2$ ). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  1927 (s). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$ , 1921 (s).

#### 2.1.2. Method B

Potassium dimethyldithiocarbamate monohydrate (0.240 g, 1.35 mmol) was added directly to a stirred

orange solution of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  (0.102 g, 0.139 mmol) in 20 ml of  $\text{CH}_2\text{Cl}_2$  and 1 ml of  $\text{MeOH}$ . The mixture was stirred for 2 h and the solvents were removed under vacuum. A procedure similar to that described above was applied, giving 76 mg of 1 (yield 68%) and 12 mg of 5 (yield 11%).

### 2.2. Preparation of *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-Et}_2\text{NCS}_2)_2]$ (2)

The yellow 2 was obtained as the only product from the reaction of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  with sodium diethyldithiocarbamate trihydrate by method B. Yield: 73%. Anal. Calc. for  $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2\text{RuS}_4$ : C, 31.77; H, 4.44; N, 6.18. Found: C, 31.68; H, 4.45; N, 6.17%.  $^1\text{H}$ -NMR (acetone- $d_6$ ):  $\delta$  1.25 (t, 6H,  $\text{CH}_3\text{CH}_2$ ,  $^3J_{\text{H,H}} = 7.2$  Hz), 1.26 (t, 6H,  $\text{CH}_3\text{CH}_2$ ,  $^3J_{\text{H,H}} = 7.2$  Hz), 3.76 (q, 4H,  $\text{CH}_3\text{CH}_2$ ,  $^3J_{\text{H,H}} = 7.2$  Hz), 3.80 (q, 4H,  $\text{CH}_3\text{CH}_2$ ,  $^3J_{\text{H,H}} = 7.2$  Hz). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  2035 (s), 1968 (s). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  2030 (s), 1952 (s).

### 2.3. Preparation of *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}^t\text{BuSCS}_2)_2]$ (3)

The orange–brown 3 was obtained as the only product from the reaction of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  with potassium *tert*-butylthioxanthate by method B. Yield: 67%. Anal. Calc. for  $\text{C}_{12}\text{H}_{18}\text{O}_2\text{RuS}_6$ : C, 29.55; H, 3.72. Found: C, 29.34; H, 3.75%.  $^1\text{H}$ -NMR (acetone- $d_6$ ):  $\delta$  1.71 (s, 18H,  $(\text{CH}_3)_3\text{C}$ ). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$ , 2051 (s), 1991 (s). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  2041 (s), 1985 (s).

### 2.4. Preparation of *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-(EtO)}_2\text{PS}_2)_2]$ (4)

The orange–yellow 4 was obtained as the only product from the reaction of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  with ammonium *O,O'*-diethyldithiophosphate by method B. Yield: 68%. Anal. Calc. for  $\text{C}_{10}\text{H}_{20}\text{O}_6\text{P}_2\text{RuS}_4$ : C, 22.77; H, 3.82. Found: C, 22.64; H, 3.87%.  $^1\text{H}$ -NMR (acetone- $d_6$ ):  $\delta$  1.33 (t, 6H,  $\text{CH}_3\text{CH}_2$ ,  $^3J_{\text{H,H}} = 7.1$  Hz), 1.37 (t, 6H,  $\text{CH}_3\text{CH}_2$ ,  $^3J_{\text{H,H}} = 7.0$  Hz), 4.22 (m, 8H,  $\text{CH}_3\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$ -NMR (acetone- $d_6$ ):  $\delta$  100.8 (s, 2P). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  2053 (s), 1987 (s).

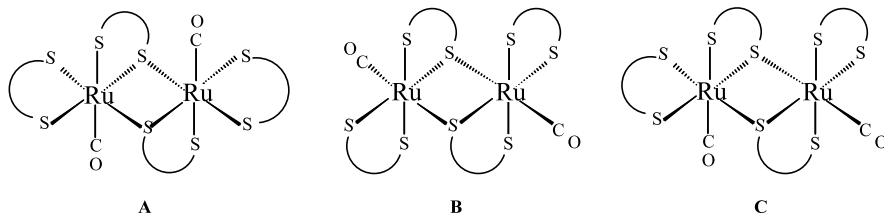


Chart 1.

Table 1  
Crystal data and structure refinement parameters for compounds **1** and **5**·CH<sub>2</sub>Cl<sub>2</sub>

Empirical formula	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> Ru <sub>2</sub> S <sub>4</sub>	C <sub>15</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> - Ru <sub>2</sub> S <sub>8</sub>
Formula weight	397.51	823.92
Temperature (K)	150(1)	150(1)
Wavelength (Mo–K <sub>α</sub> ) (Å)	0.71073	0.71073
Space group	monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	monoclinic, <i>C</i> 2/ <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	6.2803(1)	10.9628(2)
<i>b</i> (Å)	17.6427(1)	14.8235(1)
<i>c</i> (Å)	13.2120(1)	17.0111(1)
$\beta$ (°)	97.336(1)	94.159(1)
<i>V</i> (Å <sup>3</sup> )	1451.93(3)	2757.14(6)
<i>Z</i>	4	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.818	1.985
<i>F</i> (000)	792	1640
Crystal size (mm)	0.30 × 0.20 × 0.15	0.20 × 0.10 × 0.10
2 $\theta$ Range (°)	3–55	3–55
Index ranges ( <i>h</i> , <i>k</i> , <i>l</i> )	±8, ±23, ±17	±14, ±19, ±22
$\mu$ (Mo–K <sub>α</sub> ) (mm <sup>-1</sup> )	1.645	1.919
Reflections collected	9266	8254
No. of observed reflections ( <i>N</i> <sub>o</sub> )	3307 (>2 $\sigma$ )	3121 (>2 $\sigma$ )
Absorption correction	Sadabs	Sadabs
Max/min transmission	0.8015/0.6805	0.8621/0.7325
Refinement program	NRCVAX	NRCVAX
No. of reflection parameters ( <i>N</i> <sub>p</sub> )	155	147
<i>R</i> <sup>a</sup> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.0255, 0.0634	0.0631, 0.1389
Goodness-of-fit <sup>a</sup>	1.067	1.120
Weighting scheme	[ $\sigma^2(F_o)$ + 0.0016 <i>F</i> <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>	[ $\sigma^2(F_o)$ + 0.00029 <i>F</i> <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>
( $\Delta\rho$ ) <sub>max</sub> (e Å <sup>-3</sup> )	0.505	2.040
( $\Delta\rho$ ) <sub>min</sub> (e Å <sup>-3</sup> )	-0.502	-1.356

<sup>a</sup>  $R = [\sum ||F_o| - |F_c|| / \sum |F_o|]$ .  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . Goodness-of-fit =  $[\sum w(|F_o| - |F_c|)^2 / N_o - N_p]^{1/2}$ .

### 2.5. Reaction between *cis*-[Ru(CO)<sub>2</sub>( $\eta^2$ -Me<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>] (**1**) and Me<sub>3</sub>NO

Trimethylamine *N*-oxide dihydrate (0.072 g, 0.65 mmol) was added directly to a stirred yellow suspension of **1** (0.218 g, 0.55 mmol) in 20 ml of MeCN. The mixture was stirred at ambient temperature for 10 h, and the volume of the solvent was reduced to ca. 1 ml. Twenty milliliters of CH<sub>2</sub>Cl<sub>2</sub> was then added to the suspension. After filtration, the orange–brown solid was washed thoroughly with CH<sub>2</sub>Cl<sub>2</sub> (20 ml) twice and dried under vacuum to give [Ru(CO)( $\eta^2$ -Me<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>]( $\mu$ , $\eta^2$ -Me<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (**5**) (0.214 g, 95%).

### 2.6. Reaction between *cis*-[Ru(CO)<sub>2</sub>( $\eta^2$ -Et<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>] (**2**) and Me<sub>3</sub>NO

Trimethylamine *N*-oxide dihydrate (0.119 g, 1.07 mmol) was added directly to a stirred yellow suspension of **2** (0.406 g, 0.90 mmol) in 20 ml of MeCN. The

mixture was stirred at ambient temperature for 22 h, and the solvent was stripped off, giving a yellow–brown solid. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–MeOH gave yellow [Ru(CO)( $\eta^2$ -Et<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>]( $\mu$ , $\eta^2$ -Et<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub> (**6**) (0.335 g, 88%). Anal. Calc. for C<sub>22</sub>H<sub>40</sub>N<sub>4</sub>O<sub>2</sub>Ru<sub>2</sub>S<sub>8</sub>: C, 31.04; H, 4.74; N, 6.58. Found: C, 30.88; H, 4.73; N, 6.59%. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.19 (m, 9H, CH<sub>3</sub>CH<sub>2</sub>), 1.24 (m, 9H, CH<sub>3</sub>CH<sub>2</sub>), 1.37 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>), 3.45 (m, 4H, CH<sub>3</sub>CH<sub>2</sub>), 3.61 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>), 3.78 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>), 3.88 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>), 4.15 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu_{CO}$  1925 (s). IR (KBr, cm<sup>-1</sup>):  $\nu_{CO}$  1943 (s), 1924 (s).

### 2.7. Preparation of *cis*-[Ru(CO)(CNCH<sub>2</sub>Ph)( $\eta^2$ -Me<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>] (**7**)

To a stirred suspension of **5** (0.294 g, 0.357 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) 0.2 ml of PhCH<sub>2</sub>NC (ca. 1.61 mmol) was added. The mixture was stirred at ambient temperature for 3 days, and the volatile was removed under vacuum. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–MeOH gave yellow *cis*-[Ru(CO)(CNCH<sub>2</sub>Ph)( $\eta^2$ -Me<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>] (**7**) (0.165 g, 95%). Anal. Calc. for C<sub>15</sub>H<sub>19</sub>N<sub>3</sub>ORuS<sub>4</sub>: C, 37.02; H, 3.93; N, 8.63. Found: C, 36.89; H, 3.94; N, 8.63%. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>):  $\delta$  3.20 (br, 6H, Me), 3.21 (br, 6H, Me), 7.37 (m, 5H, Ph), 7.51 (d, 1H, CNCH<sub>2</sub>Ph, <sup>2</sup>*J*<sub>H,H</sub> = 7.6 Hz), 7.56 (d, 1H, CNCH<sub>2</sub>Ph, <sup>2</sup>*J*<sub>H,H</sub> = 7.6 Hz). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu_{CN}$  2109 (s);  $\nu_{CO}$  1962 (s). IR (KBr, cm<sup>-1</sup>):  $\nu_{CN}$  2105 (s);  $\nu_{CO}$  1971 (s).

### 2.8. Preparation of *cis*-[Ru(CO)(CNCH<sub>2</sub>Ph)( $\eta^2$ -Et<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>] (**8**)

To a stirred solution of **6** (0.136 g, 0.319 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) 0.2 ml of PhCH<sub>2</sub>NC (ca. 1.61 mmol) was added. The mixture was stirred at ambient temperature for 2 h, and the volatile was removed under vacuum. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–hexane gave yellow *cis*-[Ru(CO)(CNCH<sub>2</sub>Ph)( $\eta^2$ -Et<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>] (**8**) (0.169 g, 97%). Anal. Calc. for C<sub>19</sub>H<sub>27</sub>N<sub>3</sub>ORuS<sub>4</sub>: C, 42.04; H, 5.01; N, 7.74. Found: C, 41.93; H, 5.05; N, 7.73%. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.52 (m, 12H, CH<sub>3</sub>CH<sub>2</sub>), 3.96 (m, 8H, CH<sub>3</sub>CH<sub>2</sub>), 7.64 (m, 5H, Ph), 7.73 (d, 1H, CNCH<sub>2</sub>Ph, <sup>2</sup>*J*<sub>H,H</sub> = 7.2 Hz), 7.77 (d, 1H, CNCH<sub>2</sub>Ph, <sup>2</sup>*J*<sub>H,H</sub> = 7.2 Hz). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu_{CN}$ , 2105 (s);  $\nu_{CO}$ , 1958 (s). IR (KBr, cm<sup>-1</sup>):  $\nu_{CN}$ , 2089(s);  $\nu_{CO}$ , 1938 (s).

### 2.9. X-ray data collection, solution and refinement

Data were collected at 150 K in a Siemens SMART-CCD instrument, equipped with a normal focus and 3 kW sealed-tube X-ray source. The structures of **1** and **5** were solved by heavy-atom methods and refined by a full-matrix least-squares procedure using NRCVAX [6]. All the non-hydrogen atoms were refined anisotropically. The other essential details of single-crystal data

measurement and refinement are given in Table 1. One chlorine atom of  $\text{CH}_2\text{Cl}_2$  in the asymmetric unit of the crystal of **5** is disordered and two chlorine positions with 70 and 30% occupancy were assigned to Cl(1) and Cl(1'), respectively. There is a residual peak with  $2.040 \text{ e } \text{\AA}^{-3}$  in a distance of  $0.09 \text{ \AA}$  close to the Cl(1) atom on the last difference Fourier map.

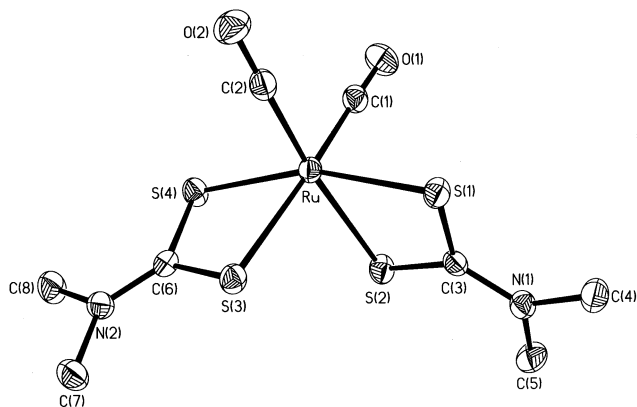


Fig. 1. ORTEP plot of **1** with 50% thermal ellipsoids. Selected bond lengths: Ru–C(1) = 1.887(3), Ru–C(2) = 1.885(3), Ru–S(1) = 2.4146(7), Ru–S(2) = 2.4586(7), Ru–S(3) = 2.4566(7), Ru–S(4) = 2.4144(7), S(1)–C(3) = 1.726(3), S(2)–C(3) = 1.724(3), S(3)–C(6) = 1.730(3), S(4)–C(6) = 1.731(3), C(1)–O(1) = 1.144(3), C(2)–O(2) = 1.151(3), N(1)–C(3) = 1.328(3), N(2)–C(6) = 1.325(3) Å. Selected bond angles: C(1)–Ru–C(2) = 91.90(11), C(1)–Ru–S(1) = 93.44(8), S(1)–Ru–S(2) = 72.46(2), S(1)–Ru–S(3) = 93.67(2), S(1)–Ru–S(4) = 161.86(2), S(2)–Ru–S(3) = 89.03(2), S(2)–Ru–S(4) = 95.11(2), S(3)–Ru–S(4) = 72.49(2), C(2)–Ru–S(4) = 93.17(8)°.

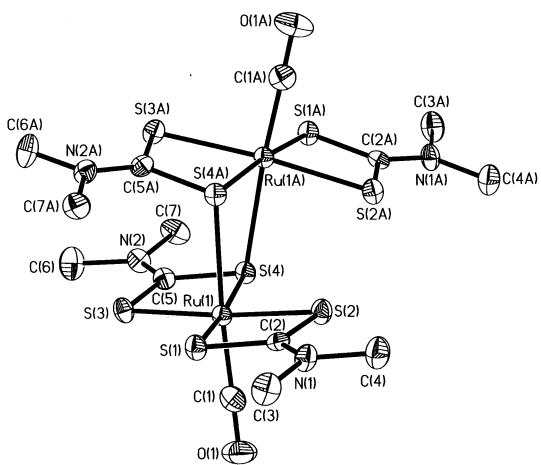


Fig. 2. ORTEP plot of **5** with 50% thermal ellipsoids. Selected bond lengths: Ru(1)–C(1) = 1.814(7), Ru(1)–S(1) = 2.395(2), Ru(1)–S(2) = 2.412(2), Ru(1)–S(3) = 2.399(2), Ru(1)–S(4) = 2.410(2), Ru(1)–S(4A) = 2.554(2), S(1)–C(2) = 1.721(7), S(2)–C(2) = 1.731(6), S(3)–C(5) = 1.701(7), S(4)–C(5) = 1.772(7), C(1)–O(1) = 1.165(9), N(1)–C(2) = 1.319(8), N(2)–C(5) = 1.324(8) Å. Selected bond angles: C(1)–Ru(1)–S(1) = 90.5(2), S(1)–Ru(1)–S(2) = 72.81(6), S(1)–Ru(1)–S(3) = 106.75(6), S(3)–Ru(1)–S(4) = 73.30(6), S(2)–Ru(1)–S(4) = 106.62(6), S(4)–Ru(1)–S(4A) = 83.16(6), Ru(1)–S(4)–Ru(1A) = 95.41(6)°.

### 3. Results and discussion

Reactions of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  or  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$  with uninegative 1,1-dithiolate anions,  $(\text{S,S})^-$ , occur as expected [1] to produce a series of mononuclear products, *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-SS})_2]$  ( $(\text{SS})^- = \text{Et}_2\text{NCS}_2^-$  (**2**),  $\text{tBuSCS}_2^-$  (**3**), and  $(\text{EtO})_2\text{PS}_2^-$  (**4**)). However, the reaction with potassium dimethyldithiocarbamate affords a mixture of two products, *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-Me}_2\text{NCS}_2)_2]$  (**1**) and  $[\text{Ru}(\text{CO})(\eta^2\text{-Me}_2\text{NCS}_2)(\mu, \eta^2\text{-Me}_2\text{NCS}_2)_2]$  (**5**), which are difficult to separate. Fortunately, after several attempts, satisfactory separation of the two products was finally achieved by the tedious fractional crystallization method. A  $^1\text{H-NMR}$  spectrum of the reaction solution after complete conversion indicated that the ratio between **1** and **5** is 3.35 and 4.63, respectively, favoring **1**. Apparently the lightly stabilized MeCN ligands of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  are replaced more readily than the bound acetate ligands of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$  by dithiolates to produce *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-SS})_2]$  with less selectivity.

Compounds **1** [7] and **2** [8] were reported earlier, but the preparation procedures, either via the direct substitution of *cis*- $[\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]$  with  $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$  or via the oxidative addition of  $[\text{Ru}_3(\text{CO})_{12}]$  with  $\text{R}_2\text{NC}(\text{S})\text{SSC}(\text{S})\text{NR}_2$  ( $\text{R} = \text{Me}, \text{Et}$ ), gave lower yields of the complexes, compared with that of ours. Like *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-S}_2\text{PMe}_2)_2]$  [1], compounds **1–4** display two carbonyl stretching bands with almost equal intensity in the IR spectra measured either in  $\text{CH}_2\text{Cl}_2$  or as a KBr disc, indicating that the two carbonyls are *cis* to each other in solution or in the solid state. Indeed, this feature is shown clearly in the solid-state structure of **1** (Fig. 1). The C–N distances of 1.328(3) and 1.325(3) Å is indicative of the presence of a partial C=N bond [9], which is found compatible with the two methyl signals observed in the  $^1\text{H-NMR}$  spectrum of **1** or **2**. The coordination environment of the metal with two mutually *cis* dithiolates is approximately octahedral with the angle, formed by two carbonyls, C(1)O(1) and C(2)O(2), as  $91.90(11)^\circ$ . Two short and two long Ru–S bonds were found ( $d(\text{Ru}–\text{S}(1)) = 2.4146(7)$  and  $d(\text{Ru}–\text{S}(4)) = 2.4144(7)$  versus  $d(\text{Ru}–\text{S}(2)) = 2.4586(7)$  and  $d(\text{Ru}–\text{S}(3)) = 2.4566(7)$  Å). Since the two long bonds are *trans* to carbonyls, the lengthening is understandable in terms of *trans* influence of the carbonyl group. However, we cannot exclude the possible involvement of the steric repulsive interactions between the dithiolate groups.

The crystal structure of **5** was also determined by X-ray diffraction methods to reveal the dimeric nature with two chelating–bridging dithiolates (Fig. 2). The molecule  $\text{CH}_2\text{Cl}_2$  was found as the solvent of crystallization. There is a crystallographically imposed  $C_2$  axis through the center of the plane defined by Ru(1),

Ru(1A), S(4), and S(4A). Hence, the structure can be described as consisting of two  $[\text{Ru}(\text{CO})(\eta^2\text{-(SS)})_2]$  fragments. It is noteworthy that the relative orientation between the two chelating dithiolates in each fragment of **5** is *trans*, rather than *cis* as observed in **1**. Hence, the structure of **5** adopts configuration **B**. This structure is kept in solution as reflected in the IR and  $^1\text{H-NMR}$  spectra; only one carbonyl stretching band was observed in solution or in the solid state, and four methyl  $^1\text{H}$  signals were observed in  $\text{CDCl}_3$ . One sulfur atom, S(4) or S(4A), of one dithiolate group in each fragment acts as the bridging atom to connect with the metal atom in the other fragment in a position *trans* to the carbonyl group. The bridging Ru–S bonding is apparently weaker with  $d(\text{Ru}(1)\text{--S}(4\text{A})) = 2.554(2)$  Å in **5**, compared with the distances of 2.4586(7) and 2.4566(7) Å for similar bonds found in **1**. Two such weak bridging bonding interactions in **5** is probably caused by the nonbonded repulsive interactions between the dithiolate groups in different fragment. As a result, the C–N distances of 1.319(8) and 1.324(8) Å in **5** are not significantly different from those in **1**.

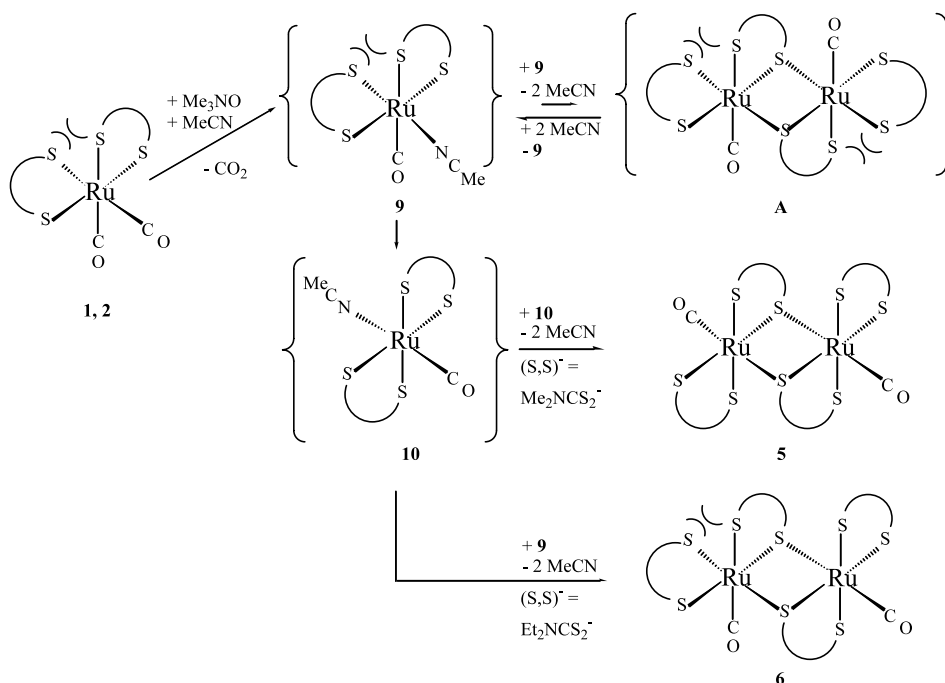
Compound **5** can be prepared alternatively via decarbonylation of **1**, using trimethylamine *N*-oxide in MeCN. However, the dimer  $[\text{Ru}(\text{CO})(\eta^2\text{-Et}_2\text{NCS}_2)(\mu, \eta^2\text{-Et}_2\text{NCS}_2)]_2$  (**6**), prepared from a similar decarbonylation reaction of **2** with  $\text{Me}_3\text{NO}$ , has a structure different from **5**. Rather complicated  $^1\text{H-NMR}$  signals were observed with three resolved multiplets in an integration ratio of 9:9:6 at  $\delta$  1.19, 1.24, and 1.37, respectively. Apparently there are more than four methyl signals observed for **6**. Though this compound displays in the IR spectrum one broad and strong carbonyl stretching band at  $1925\text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ , it shows two sharp such bands at 1943 and  $1924\text{ cm}^{-1}$  with almost equal intensity in the solid state. The broad band at  $1925\text{ cm}^{-1}$  is probably caused by the overlapping of two bands at a close wave number. All these spectral evidences may suggest another configuration for **6**, probably configuration **C**. However, both **5** and **6** reacts readily at ambient temperature with benzyl isocyanide to yield a product with a similar geometry,  $\text{cis-}[\text{Ru}(\text{CO})(\text{CNCH}_2\text{Ph})(\eta^2\text{-(SS)})_2]$  ( $(\text{SS})^- = \text{Me}_2\text{NCS}_2^-$  (**7**) and  $\text{Et}_2\text{NCS}_2^-$  (**8**)). The *cis* assignment is based on one set of the **AB** quartet observed in the  $^1\text{H-NMR}$  spectrum assigned to the benzyl hydrogen nuclei for **7** or **8**.

Various kinds of structure for mono- and dinuclear compounds can be explained in terms of both electronic and steric factors. The steric repulsive interactions are believed to be present between any two *cis* chelating dithiolates in either mono- or dinuclear complexes. However, two strong  $\pi$ -acceptor ligands in all mononuclear species (i.e. two COs in **1–4** and one CO and one RNC in **7–8**) prefer to locate at *cis* positions on an octahedral coordination sphere around the Ru atom to help releasing the accumulated charge density of the Ru

complexes of two strong  $\sigma$ -donor ligands, dithiolates, via back donation. The electronic factor, rather than the steric factor, determines the *cis*-geometry as observed in **1–4** and **7–8**. Thus, once the decarbonylation of  $\text{cis-}[\text{Ru}(\text{CO})_2(\eta^2\text{-(SS)})_2]$  (**1** and **2**) occurred in MeCN and the resulting intermediate  $\text{cis-}[\text{Ru}(\text{CO})(\text{NCMe})(\eta^2\text{-(SS)})_2]$  (**9**) with only one  $\pi$ -acceptor, CO, formed, this intermediate isomerizes to relieve the steric congestion between the two *cis* chelating dithiolates and form  $\text{trans-}[\text{Ru}(\text{CO})(\text{NCMe})(\eta^2\text{-(SS)})_2]$  (**10**). The subsequent replacement of MeCN of **10** with a strong donating dithiolate of another species, **10** or **9**, forms a dimer  $[\text{Ru}(\text{CO})(\eta^2\text{-(S,S)})(\mu, \eta^2\text{-(S,S)})_2]$  ( $(\text{SS})^- = \text{Me}_2\text{NCS}_2^-$  (**5**) or  $\text{Et}_2\text{NCS}_2^-$  (**6**)) in configuration **B** or **C**, respectively (Scheme 1). The mononuclear intermediate  $\text{trans-}[\text{Ru}(\text{CO})(\text{CNCH}_2\text{Ph})(\eta^2\text{-(SS)})_2]$  (**11**), if produced during the reaction of **5** and **6** with benzyl isocyanide in  $\text{CH}_2\text{Cl}_2$ , isomerize into  $\text{cis-}[\text{Ru}(\text{CO})(\text{CNCH}_2\text{Ph})(\eta^2\text{-(SS)})_2]$  ( $(\text{SS})^- = \text{Me}_2\text{NCS}_2^-$  (**7**),  $\text{Et}_2\text{NCS}_2^-$  (**8**)). It is apparent that **11** is a kinetic product while **7** and **8** are thermodynamic products. No dinuclear products in configuration **A** was observed, probably indicating that the steric repulsive interactions between the two mutually *cis* dithiolates in  $\text{cis-}[\text{Ru}(\text{CO})(\text{NCMe})(\eta^2\text{-(SS)})_2]$  are slightly larger than that in  $\text{cis-}[\text{Ru}(\text{CO})_2(\eta^2\text{-(SS)})_2]$ . Such repulsion may be increased appreciably during the dimerization, thus weakening the dimerization of  $\text{cis-}[\text{Ru}(\text{CO})(\text{NCMe})(\eta^2\text{-(SS)})_2]$  into  $[\text{Ru}(\text{CO})(\eta^2\text{-(S,S)})(\mu, \eta^2\text{-(S,S)})_2]$  in configuration **A**, a feature reminiscent of the **B** (back) strain in influencing the acid–base interaction [10].

#### 4. Conclusion

The reaction of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  or  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$  with potassium dimethyldithiocarbamate, sodium diethyldithiocarbamate, potassium *tert*-butylthioxanthate, and ammonium *O,O'*-diethylthiophosphate gives both mono- and dimeric products of  $\text{cis-}[\text{Ru}(\text{CO})_2(\eta^2\text{-(SS)})_2]$  (**1–4**) and  $[\text{Ru}(\text{CO})(\eta^2\text{-Me}_2\text{NCS}_2)(\mu, \eta^2\text{-Me}_2\text{NCS}_2)]_2$  (**5**) with two structures **1** and **5** determined (Fig. 1 Fig. 2). The lightly stabilized MeCN ligands of  $[\text{Ru}_2(\text{CO})_4(\text{MeCN})_6][\text{BF}_4]_2$  are replaced more readily than the bound acetate ligands of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeCN})_2]$  by dithiolates to produce  $\text{cis-}[\text{Ru}(\text{CO})_2(\eta^2\text{-(SS)})_2]$  with less selectivity. Two dinuclear products **5** and **6** can also be prepared from the decarbonylation reaction of  $\text{cis-}[\text{Ru}(\text{CO})_2(\eta^2\text{-R}_2\text{NCS}_2)]_2$  ( $\text{R} = \text{Me}$  (**1**) and  $\text{Et}$  (**2**)) with  $\text{Me}_3\text{NO}$ . Although structure **5** adopts configuration **B**, structure **6** takes configuration **C**. Both **5** and **6** react readily at ambient temperature with benzyl isocyanide to yield  $\text{cis-}[\text{Ru}(\text{CO})(\text{CNCH}_2\text{Ph})(\eta^2\text{-R}_2\text{NCS}_2)]_2$  ( $\text{R} = \text{Me}$  (**7**) and  $\text{Et}$  (**8**)). A dimerization pathway for  $\text{cis-}[\text{Ru}(\text{CO})_2(\eta^2\text{-}$



Scheme 1.

$(\text{SS})_2]$  via decarbonylation and isomerization is proposed (Scheme 1).

## 5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 173452 and 173453 for compounds **1** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

## Acknowledgements

The authors thank the National Science Council of the Republic of China for financial support of this research (Contract No. NSC89-2113-M006-013).

## References

- [1] R.W. Hiltz, M. Cowie, *Inorg. Chem.* 29 (1990) 3349.
- [2] (a) K.-B. Shiu, C.-H. Li, T.-J. Chan, S.-M. Peng, M.-C. Cheng, S.-L. Wang, F.-L. Liao, M.Y. Chiang, *Organometallics* 14 (1995) 524; (b) K.-B. Shiu, L.-T. Yang, S.-W. Jean, C.-H. Li, R.-R. Wu, J.-C. Wang, L.-S. Liou, M.Y. Chiang, *Inorg. Chem.* 35 (1996) 7845.
- [3] J. Powell, M.J. Horvath, *Organometallics* 12 (1993) 4067.
- [4] A. Author, in: F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann (Eds.), *Advanced Inorganic Chemistry*, sixth ed., Wiley, New York, 1999, p. 541.
- [5] G.R. Crooks, G. Gamlen, B.F.G. Johnson, J. Lewis, I.G. Williams, *J. Chem. Soc. A* (1969) 2761.
- [6] E.J. Gabe, Y. Le page, J.-P. Charland, F.L. Lee, P.S. Lee, *J. Appl. Crystallogr.* 22 (1989) 384.
- [7] D.J. Cole-Hamilton, T.A. Stephenson, *J. Chem. Soc. Dalton Trans.* (1974) 739.
- [8] A.J. Deeming, R. Vaish, *J. Organomet. Chem.* 460 (1993) C8.
- [9] K.-B. Shiu, S.-T. Lin, S.-M. Peng, M.-C. Cheng, *Inorg. Chim. Acta* 229 (1995) 153.
- [10] H.C. Brown, *J. Chem. Soc.* (1956) 1248.