

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

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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**), 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 Me_3NO 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 Me_3NO , 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**), 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 CH_2Cl_2 molecule as one chloro ligand around Ru [3], or a dinuclear product, as a CH_2Cl_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.

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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. ^1H - and ^{31}P -NMR spectra were recorded in a Bruker AMC400 spectrometer (^1H , 400 MHz; ^{31}P , 162 MHz) calibrated against internal deuterated solvents (^1H) or external 85% H_3PO_4 (^{31}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 Et_2O – 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 CH_2Cl_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%. ^1H -NMR (CDCl_3): δ 3.26 (s, 6H, Me), 3.28 (s, 6H, Me). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2039 (s), 1972 (s). IR (KBr, cm^{-1}): ν_{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%. ^1H -NMR (CDCl_3): δ 3.22 (br, 6H, Me), 3.36 (br, 6H, Me), 3.60 (br, 6H, Me), 3.62 (br, 6H, Me), 5.32 (s, 2H, CH_2Cl_2). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 1927 (s). IR (KBr, cm^{-1}): ν_{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 CH_2Cl_2 and 1 ml of 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%. ^1H -NMR (acetone- d_6): δ 1.25 (t, 6H, CH_3CH_2 , $^3J_{\text{H,H}} = 7.2$ Hz), 1.26 (t, 6H, CH_3CH_2 , $^3J_{\text{H,H}} = 7.2$ Hz), 3.76 (q, 4H, CH_3CH_2 , $^3J_{\text{H,H}} = 7.2$ Hz), 3.80 (q, 4H, CH_3CH_2 , $^3J_{\text{H,H}} = 7.2$ Hz). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2035 (s), 1968 (s). IR (KBr, cm^{-1}): ν_{CO} 2030 (s), 1952 (s).

2.3. Preparation of *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}^i\text{BuSCS}_2)_2]$ (**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%. ^1H -NMR (acetone- d_6): δ 1.71 (s, 18H, $(\text{CH}_3)_3\text{C}$). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} , 2051 (s), 1991 (s). IR (KBr, cm^{-1}): ν_{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%. ^1H -NMR (acetone- d_6): δ 1.33 (t, 6H, CH_3CH_2 , $^3J_{\text{H,H}} = 7.1$ Hz), 1.37 (t, 6H, CH_3CH_2 , $^3J_{\text{H,H}} = 7.0$ Hz), 4.22 (m, 8H, CH_3CH_2). $^{31}\text{P}\{^1\text{H}\}$ -NMR (acetone- d_6): δ 100.8 (s, 2P). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 2053 (s), 1987 (s).

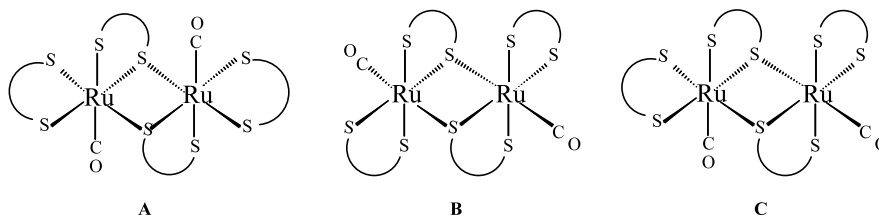


Chart 1.

Table 1
Crystal data and structure refinement parameters for compounds **1** and **5**·CH₂Cl₂

Empirical formula	C ₈ H ₁₂ N ₂ O ₂ Ru ₂ S ₄	C ₁₅ H ₂₆ Cl ₂ N ₄ O ₂ - Ru ₂ S ₈
Formula weight	397.51	823.92
Temperature (K)	150(1)	150(1)
Wavelength (Mo–K _α) (Å)	0.71073	0.71073
Space group	monoclinic, <i>P</i> 2 ₁ / <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)
β (°)	97.336(1)	94.159(1)
<i>V</i> (Å ³)	1451.93(3)	2757.14(6)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	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 θ Range (°)	3–55	3–55
Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	±8, ±23, ±17	±14, ±19, ±22
μ (Mo–K _α) (mm ⁻¹)	1.645	1.919
Reflections collected	9266	8254
No. of observed reflections (<i>N</i> _o)	3307 (>2 σ)	3121 (>2 σ)
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> _p)	155	147
<i>R</i> ^a , <i>R</i> _w ^a	0.0255, 0.0634	0.0631, 0.1389
Goodness-of-fit ^a	1.067	1.120
Weighting scheme	[$\sigma^2(F_o)$ + 0.0016 <i>F</i> _o ²] ⁻¹	[$\sigma^2(F_o)$ + 0.00029 <i>F</i> _o ²] ⁻¹
($\Delta\rho$) _{max} (e Å ⁻³)	0.505	2.040
($\Delta\rho$) _{min} (e Å ⁻³)	-0.502	-1.356

^a *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)₂(η^2 -Me₂NCS₂)₂] (**1**) and Me₃NO

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 CH₂Cl₂ was then added to the suspension. After filtration, the orange–brown solid was washed thoroughly with CH₂Cl₂ (20 ml) twice and dried under vacuum to give [Ru(CO)(η^2 -Me₂NCS₂)₂](μ , η^2 -Me₂NCS₂)₂·CH₂Cl₂ (**5**) (0.214 g, 95%).

2.6. Reaction between *cis*-[Ru(CO)₂(η^2 -Et₂NCS₂)₂] (**2**) and Me₃NO

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 CH₂Cl₂–MeOH gave yellow [Ru(CO)(η^2 -Et₂NCS₂)₂](μ , η^2 -Et₂NCS₂)₂ (**6**) (0.335 g, 88%). Anal. Calc. for C₂₂H₄₀N₄O₂Ru₂S₈: C, 31.04; H, 4.74; N, 6.58. Found: C, 30.88; H, 4.73; N, 6.59%. ¹H-NMR (CD₂Cl₂): δ 1.19 (m, 9H, CH₃CH₂), 1.24 (m, 9H, CH₃CH₂), 1.37 (m, 6H, CH₃CH₂), 3.45 (m, 4H, CH₃CH₂), 3.61 (m, 2H, CH₃CH₂), 3.78 (m, 6H, CH₃CH₂), 3.88 (m, 2H, CH₃CH₂), 4.15 (m, 2H, CH₃CH₂). IR (CH₂Cl₂, cm⁻¹): ν_{CO} 1925 (s). IR (KBr, cm⁻¹): ν_{CO} 1943 (s), 1924 (s).

2.7. Preparation of *cis*-[Ru(CO)(CNCH₂Ph)(η^2 -Me₂NCS₂)₂] (**7**)

To a stirred suspension of **5** (0.294 g, 0.357 mmol) in CH₂Cl₂ (50 ml) 0.2 ml of PhCH₂NC (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 CH₂Cl₂–MeOH gave yellow *cis*-[Ru(CO)(CNCH₂Ph)(η^2 -Me₂NCS₂)₂] (**7**) (0.165 g, 95%). Anal. Calc. for C₁₅H₁₉N₃ORuS₄: C, 37.02; H, 3.93; N, 8.63. Found: C, 36.89; H, 3.94; N, 8.63%. ¹H-NMR (acetone-*d*₆): δ 3.20 (br, 6H, Me), 3.21 (br, 6H, Me), 7.37 (m, 5H, Ph), 7.51 (d, 1H, CNCH₂Ph, ²*J*_{H,H} = 7.6 Hz), 7.56 (d, 1H, CNCH₂Ph, ²*J*_{H,H} = 7.6 Hz). IR (CH₂Cl₂, cm⁻¹): ν_{CN} 2109 (s); ν_{CO} 1962 (s). IR (KBr, cm⁻¹): ν_{CN} 2105 (s); ν_{CO} 1971 (s).

2.8. Preparation of *cis*-[Ru(CO)(CNCH₂Ph)(η^2 -Et₂NCS₂)₂] (**8**)

To a stirred solution of **6** (0.136 g, 0.319 mmol) in CH₂Cl₂ (15 ml) 0.2 ml of PhCH₂NC (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 CH₂Cl₂–hexane gave yellow *cis*-[Ru(CO)(CNCH₂Ph)(η^2 -Et₂NCS₂)₂] (**8**) (0.169 g, 97%). Anal. Calc. for C₁₉H₂₇N₃ORuS₄: C, 42.04; H, 5.01; N, 7.74. Found: C, 41.93; H, 5.05; N, 7.73%. ¹H-NMR (CD₂Cl₂): δ 1.52 (m, 12H, CH₃CH₂), 3.96 (m, 8H, CH₃CH₂), 7.64 (m, 5H, Ph), 7.73 (d, 1H, CNCH₂Ph, ²*J*_{H,H} = 7.2 Hz), 7.77 (d, 1H, CNCH₂Ph, ²*J*_{H,H} = 7.2 Hz). IR (CH₂Cl₂, cm⁻¹): ν_{CN} , 2105 (s); ν_{CO} , 1958 (s). IR (KBr, cm⁻¹): ν_{CN} , 2089(s); ν_{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 CH_2Cl_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 \AA close to the Cl(1) atom on the last difference Fourier map.

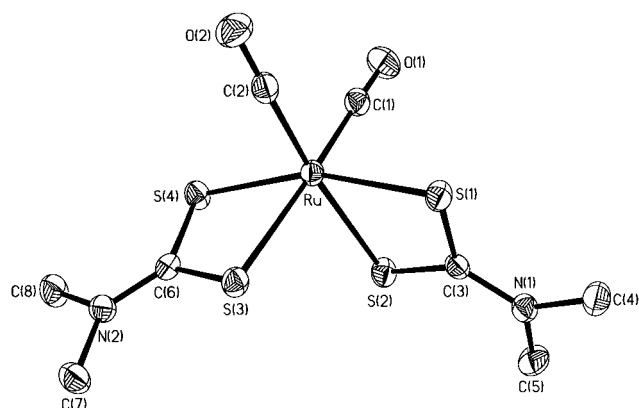


Fig. 1. ORTEP plot of **1** with 50% thermal ellipsoids. Selected bond lengths: Ru–C(1) = 1.887(3), Ru–C(2) = 1.885(3), Ru–S(1) = 2.4146(7), Ru–S(2) = 2.4586(7), Ru–S(3) = 2.4566(7), Ru–S(4) = 2.4144(7), S(1)–C(3) = 1.726(3), S(2)–C(3) = 1.724(3), S(3)–C(6) = 1.730(3), S(4)–C(6) = 1.731(3), C(1)–O(1) = 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)°.

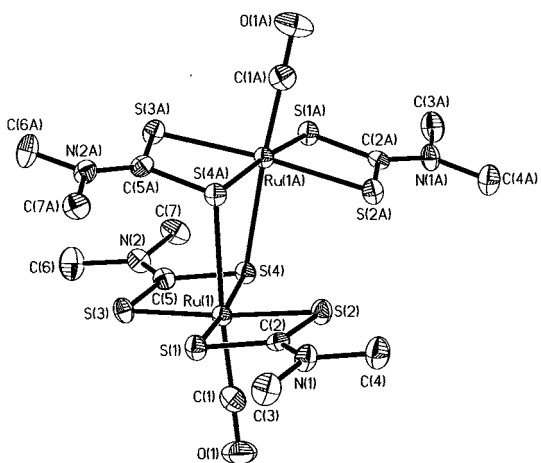


Fig. 2. ORTEP plot of **5** with 50% thermal ellipsoids. Selected bond lengths: Ru(1)–C(1) = 1.814(7), Ru(1)–S(1) = 2.395(2), Ru(1)–S(2) = 2.412(2), Ru(1)–S(3) = 2.399(2), Ru(1)–S(4) = 2.410(2), Ru(1)–S(4A) = 2.554(2), S(1)–C(2) = 1.721(7), S(2)–C(2) = 1.731(6), S(3)–C(5) = 1.701(7), S(4)–C(5) = 1.772(7), 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, $(\text{S},\text{S})^-$, occur as expected [1] to produce a series of mononuclear products, *cis*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}(\text{SS}))_2]$ ($(\text{SS})^- = \text{Et}_2\text{NCS}_2^-$ (**2**), 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*- $[\text{Ru}(\text{CO})_2(\eta^2\text{-}(\text{SS}))_2]$ 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 $\text{R}_2\text{NC}(\text{S})\text{SSC}(\text{S})\text{NR}_2$ (R = Me, 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 CH_2Cl_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 CH_2Cl_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 ^1H signals were observed in 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**.

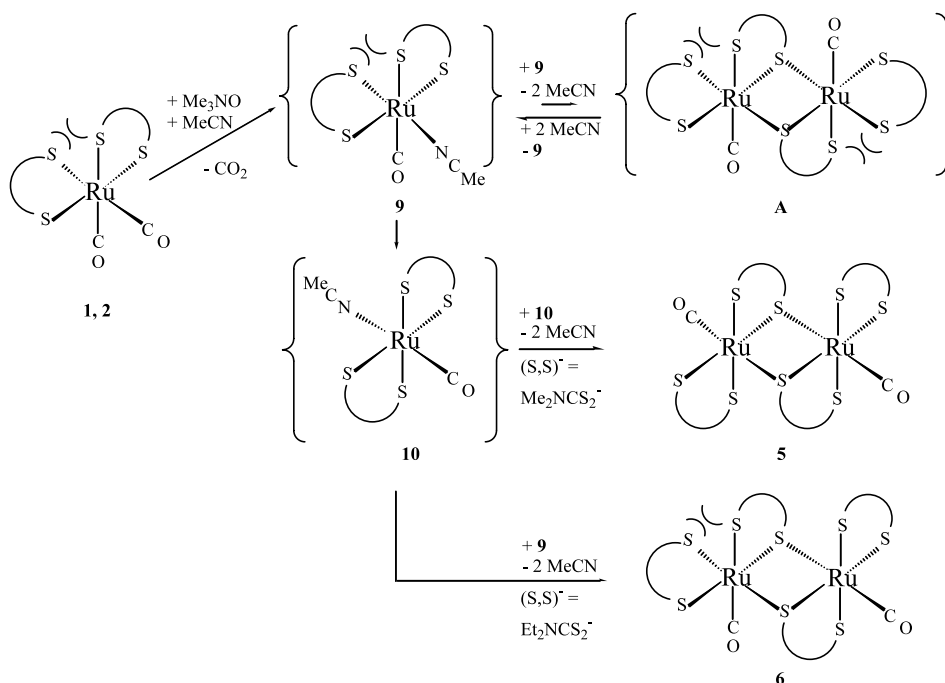
Compound **5** can be prepared alternatively via decarbonylation of **1**, using trimethylamine *N*-oxide in MeCN. However, the dimer $[\text{Ru}(\text{CO})(\eta^2\text{-Et}_2\text{NCS}_2)(\mu, \eta^2\text{-Et}_2\text{NCS}_2)]_2$ (**6**), prepared from a similar decarbonylation reaction of **2** with Me_3NO , 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 δ 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 cm^{-1} in CH_2Cl_2 , it shows two sharp such bands at 1943 and 1924 cm^{-1} with almost equal intensity in the solid state. The broad band at 1925 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 π -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 σ -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 π -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 CH_2Cl_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 Et (**2**)) with Me_3NO . 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 Et (**8**)). A dimerization pathway for $\text{cis-}[\text{Ru}(\text{CO})_2(\eta^2\text{-}$



Scheme 1.

(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>).

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