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Note

# Synthesis and characterization of ruthenium 'pincer' complexes containing sulfur atom donor ligands. The X-ray crystal structure of $[RuCl_2(\eta^3\text{-}NN'N)(SMe_2)]$ ($NN'N = \{2,6\text{-}(Me_2NCH_2)_2C_5H_3N\}$)

Ignacio del Río [a], Robert A. Gossage [a,1], Martin Lutz [b], Anthony L. Spek [b,2], Gerard van Koten [a,*]

[a] *Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands*
[b] *The Bijvoet Center for Biomolecular Research, Laboratory of Crystal Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

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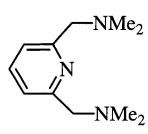
**Abstract**

The reaction of dialkylsulfides or sulfur dioxide with $[Ru_2Cl_4(\eta^3\text{-}NN'N)_2(\mu\text{-}N_2)]$ (**1**: $NN'N = \{2,6\text{-}(Me_2NCH_2)_2C_5H_3N\}$) leads to the formation of mononuclear complexes of the general formula $[RuCl_2(\eta^3\text{-}NN'N)(\eta^1\text{-}SR_2)]$ ($SR_2 = SMe_2$, $SEt_2$, $C_4H_8S$, $SO_2$). Related dialkyldisulfides and sterically hindered sulfides or thiophenes do not react with **1** or form complicated mixtures of compounds. The X-ray crystal structure of the dimethylsulfide complex $[RuCl_2(\eta^3\text{-}NN'N)_2(SMe_2)]$, is reported. © 1999 Elsevier Science S.A. All rights reserved.

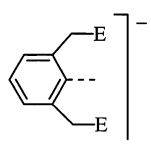
*Keywords:* Crystal structures; Ruthenium complexes; Pincer complexes; Sulfur ligand complexes

## 1. Introduction

In a series of publications, we have reported a large number of transition metal (TM) and lanthanide complexes containing multidentate donor fragments that are commonly referred to as 'pincer' ligands [1]. These species include such organic molecules as 2,6-bis-[(dimethylamino)methyl]pyridine (NN′N) [2], 3,5-bis-[(dimethylamino)methyl]pyridine [3] and the aryl carbanions derived from 2,6-bis[(dimethylamino)methyl]-benzene (NCN′) [1,4] or its phosphorous analogues (PCP: Fig. 1) [5]. Specifically, we have recently concentrated on the chemistry of ruthenium and have found a number of interesting catalytic [6] and electrochemical properties [7] as well as unusual bonding motifs of pincer ligands [8] in complexes containing this metal atom. As our interests lie in the direction of TM-mediated organic synthesis [9] and molecular sensor technology [10], we have embarked on a study of the coordination chemistry of sulfur containing environmental pollutants such as alkylsulfides and sulfur dioxide [10]. The overall goal of this work is aimed at the detection and catalytic destruction of these toxic, malodorous and hazardous compounds.




NN′N




$[NCN]^-$: E = $NMe_2$; $[PCP]^-$: E = $PR_2$

Fig. 1.

* Corresponding author. Tel.: +31-30-253 3120; fax: +31-30-252 3615.

*E-mail address:* g.vankoten@chem.uu.nl (G. van Koten)

[1] Present address: AnorMED Inc., #100 20353 64th Avenue, Langley, BC, V2Y 1N5 Canada.

[2] Author to whom correspondence should be directed pertaining to the crystallographic section of this manuscript (e-mail: a.l.spek@chem.uu.nl).



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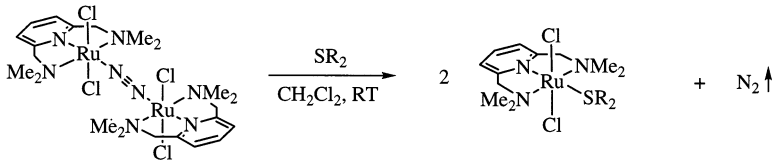


| Comp. | $SR_2$ |
|---|---|
| **2** | $SMe_2$ |
| **3** | $SEt_2$ |
| **4** | $SC_4H_8$ |
| **5** | $SO_2$ |

Scheme 1.

In this report, we detail our study of the reactivity and coordination chemistry of sulfides with a Ru fragment containing the NN′N ligand. This work reveals that the dinitrogen-bridged complex $[Ru_2Cl_4(NN'N)_2(\mu\text{-}N_2)]$ (**1**: Scheme 1) readily reacts with simple divalent sulfides or sulfur dioxide to yield the corresponding mononuclear derivatives $[RuCl_2(NN'N)(SR_2)]$ ($SR_2 =$ $SMe_2$, $SEt_2$, $C_4H_8S$, $SO_2$) in excellent overall yields. In addition, we detail the solid-state structure, obtained via a single crystal X-ray diffraction study, of the complex $[RuCl_2(\eta^3\text{-}NN'N)(SMe_2)]$ (**2**).

## 2. Results and discussion

We have previously reported on the dinuclear complex $[Ru_2Cl_4(NN'N)_2(\mu\text{-}N_2)]$ (**1**), which can be obtained in high yield by the simple treatment of $[RuCl_2(nbd)]_n$ (nbd = 1,5-norbornadiene) with NN′N under a dinitrogen atmosphere [11]. Compound **1** is very reactive under mild conditions with a vast array of neutral donor ligands such as tertiary phosphines [12a], CO [11], alkynes and alkenes [12b]. Thus, the reactivity of **1** with sulfur containing nucleophiles was undertaken.

Treatment of a dichloromethane solution of **1** with dimethyl or diethylsulfide leads to the formation of the corresponding mononuclear complexes $[RuCl_2(\eta^3\text{-}NN'N)(SR_2)]$ (**2**: R = Me; **3**: R = Et, Scheme 1) in high yield and purity. The solution structure of these two compounds is strongly suggested by examination of their NMR spectra ($^1H$ and $^{13}C\{^1H\}$), which indicate that both $-NMe_2$ groups are still coordinated to the metal [2,11] and that the $SMe_2$ ligand is coordinated and in average bisected by a symmetry plane. The molecular $C_{2v}$ symmetry of the $[RuCl_2(\eta^3\text{-}NN'N)]$ fragment is confirmed by the signals observed for the $CH_2$ and $NMe_2$ groups of the pyridine ligand, both of which appear as singlets ($\delta = 3.97$ and 2.44, respectively). These data reflect the dynamic nature of these complexes, involving inversion at the coordinated sulfur atom, a process frequently observed for similar complexes [13]. To further confirm that this structural motif is retained in the solid state, a single crystal X-ray diffraction study of **2** was carried out[3]. This revealed that the general structure suggested in solution is also found in the solid state. A molecular plot of **2** is depicted in Fig. 2 with pertinent bond lengths and

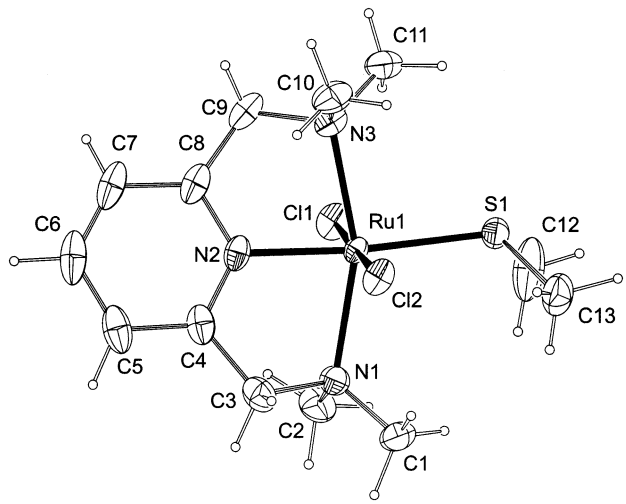


Fig. 2. Molecular structure of compound **2**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), angles and torsion angles (°): Ru(1)–Cl(1), 2.4249(7); Ru(1)–Cl(2), 2.4381(7); Ru(1)–N(1), 2.194(2); Ru(1)–N(2), 1.978(2); Ru(1)–N(3), 2.188(2); Ru(1)–S(1), 2.3572(7); S(1)–C(12), 1.794(4); S(1)–C(13), 1.790(3); Cl(1)–Ru(1)–Cl(2), 179.25(3); Cl(1)–Ru(1)–S(1), 89.57(2); Cl(2)–Ru(1)–S(1), 90.12(2); S(1)–Ru(1)–N(1), 105.40(6); S(1)–Ru(1)–N(2), 174.45(7); S(1)–Ru(1)–N(3), 94.88(6); Ru(1)–S(1)–C(12), 112.46(14); Ru(1)–S(1)–C(13), 114.72(11); C(12)–S(1)–C(13), 99.0(2); N(2)–C(8)–C(9)–N(3), −28.0(3); N(2)–C(4)–C(3)–N(1), −33.0(3).

[3] Crystal and refinement data for **2**: dark red plates, 0.019 × 0.2 × 0.3 mm; formula: $C_{13}H_{25}Cl_2N_3RuS$; MW = 427.39; $a = 14.8638(12)$, $b = 7.8525(6)$, $c = 16.0628(9)$ Å; $\beta = 112.705(6)°$; $V = 1729.5(2)$ Å$^3$; monoclinic, space group $P2_1/c$, $Z = 4$; Temperature = 200 K; Enraf–Nonius CAD4T diffractometer with rotating anode ($\lambda = 0.71073$ Å); ω-scans; corrections for Lorentz-polarization effects and absorption (analytical, $T = 53$–95%); 8105 measured reflections, 3981 unique reflections; 281 parameters; $R_1$ ($F$, observed reflections) = 0.0309; $wR_2$ ($F^2$, all reflections) = 0.0577; structure solution with Patterson methods (DIRDIF96 [15]); structure refinement with SHELXL-97 [16].

angles listed in the figure caption. The Ru atom is hexacoordinated in a distorted octahedral ligand environment with the three N donor atoms in a meridional configuration. In contrast to the perfect meridional geometry, **2** possesses no mirror plane, because of the non-planarity of the NN′N ligand. Additionally, there is an interplanar angle of 14.8(2)° of the pyridine ring to the plane N(1)–Ru(1)–N(3), which also breaks the mirror symmetry. The S atom is bonded *trans* to the pyridine nitrogen atom, a situation which forces the two chlorine atoms to be positioned *trans* to one another. Bond lengths and angles are typical when compared with related structures [1,4c,4d,5,7,8b,11,14]. Full structural details can be found in Section 5.

Similar treatment of **1** with tetrahydrothiophene gave **4**, an analogue of **2** or **3**, but this species was not stable enough to isolate and could only be observed in situ by NMR spectroscopy (vide infra). Complex **1** did not react with phenyl substituted sulfides, thiophene, elemental sulfur, dialkyl nor diaryl disulfides. The addition of hydrogen sulfide to **1** led to decomposition.

Sulfur dioxide gas does react with **1** to form a stable complex, **5**, in good yield. The attachment of $SO_2$ does not appear to be readily reversible, in contrast to our related Pt(II) systems [10]. Characterization of this complex by NMR, FAB MS and elemental analyses can be found in Section 4.

## 3. Conclusions

The reactivity of the dinitrogen-bridged complex $[Ru_2Cl_4(\eta^3\text{-NN}'\text{N})_2(\mu\text{-N}_2)]$ (**1**) with simple dialkylsulfides and sulfur dioxide has been demonstrated. The X-ray crystal structure of the dimethylsulfide adduct has been determined. Electron poor sulfides or dialkyldisulfides do not react with **1** or lead to decomposition. Sulfur dioxide forms a stable complex on reaction with **1**. We are currently studying the reactivity of the coordinated sulfur ligands, with the intention of investigating the activation of these fragments.

## 4. Experimental

### 4.1. General data

Instrumentation and general procedures were carried out as reported previously [11,12]. Complex **1** was prepared as described earlier [11].

### 4.2. Synthesis of $[RuCl_2(\eta^3\text{-NN}'\text{N})(SMe_2)]$ (2)

An excess of dimethylsulfide (ca. 0.1 ml) was added to a solution of **1** (50 mg, 0.066 mmol) in $CH_2Cl_2$ (30 ml) and the mixture was then stirred at room temperature (r.t.) for 15 min. The colour changed from orange to dark red. The solvent was removed under reduced pressure and the residue washed with pentane (2 × 20 ml) to give **2** as a red solid (50 mg, 89%). *Anal.* Calc. for $C_{13}H_{25}Cl_2N_3RuS$ (427.4): C, 36.53; H, 5.90; N, 9.83. Found: C, 36.40; H, 5.85; N, 9.91%. FAB-MS: 427 ([$M^+$]). $^1$H NMR ($CDCl_3$): 7.51 (t, $J = 7.8$, Ar*H*), 7.22 (d, $J = 7.8$, Ar*H*), 3.97 (s, $CH_2$), 2.56 (s, $SMe_2$), 2.44 (s, $NMe_2$); $^{13}C\{^1H\}$ ($CDCl_3$): 163.6, 132.6, 119.2 (Ar*C*′s), 72.8 ($CH_2$), 55.1 ($NMe_2$), 21.9 ($SMe_2$).

### 4.3. Synthesis of $[RuCl_2(\eta^3\text{-NN}'\text{N})(SEt_2)]$ (3)

An excess of diethylsulfide (ca. 0.1 ml) was added to a solution of **1** (50 mg, 0.066 mmol) in $CH_2Cl_2$ (30 ml) and the mixture was then stirred at r.t. for 15 min. The colour changed from orange to dark red. The solvent was removed under reduced pressure and the residue washed with pentane (2 × 20 ml) to give **3** as a red solid (50 mg, 89%). *Anal.* Calc. for $C_{15}H_{32}Cl_2N_3RuS$: C, 39.55; H, 6.42; N, 9.23. Found: C, 39.72; H, 6.55; N, 9.23%. $^1$H NMR ($CDCl_3$): 7.51 (t, $J = 7.8$, Ar*H*), 7.22 (d, $J = 7.8$, Ar*H*), 3.99 (s, $CH_2$), 3.10 (q, $J = 7.4$, $SCH_2$), 2.51 (s, $NMe_2$), 1.50 (t, $J = 7.4$, $SCH_2CH_3$); $^{13}C\{^1H\}$ ($CDCl_3$): 161.8, 130.6, 117.3 (Ar*C*′s), 71.0 ($CH_2$), 53.4 ($NMe_2$), 26.7 ($SCH_2$), 13.3 (Me).

### 4.4. Synthesis of $[RuCl_2(\eta^3\text{-NN}'\text{N})(THT)]$ (4)

An excess of tetrahydrothiophene (ca. 0.5 ml) was added to a solution of **1** (200 mg, 0.264 mmol) in $CH_2Cl_2$ (40 ml) and the mixture was then stirred at r.t. for 30 min. The colour changed from orange to brown. The solvent was removed under reduced pressure and the residue washed with ether/hexane (1:1 v/v, 2 × 20 ml) to give **4** as a brown solid (140 mg, 88%). This material was further analysed by NMR spectroscopy. Several attempts to purify **4** by recrystallization were not successful. $^1$H NMR ($CDCl_3$): 7.55 (t, $J = 7.2$, Ar*H*), 7.26 (d, $J = 7.2$, Ar*H*), 4.02 (s, $CH_2$), 3.30 (m, $SCH_2$), 2.48 (s, $NMe_2$), 2.22 (m, $CH_2$); $^{13}C\{^1H\}$ ($CDCl_3$): 161.1, 130.2, 116.9 (Ar*C*′s), 70.5 ($CH_2$), 55.8 ($NMe_2$), 33.2 ($SCH_2$), 28.3 ($CH_2$).

### 4.5. Synthesis of $[RuCl_2(\eta^3\text{-NN}'\text{N})(SO_2)]$ (5)

Sulfur dioxide gas was bubbled through a solution of **1** (150 mg, 0.066 mmol) in $CH_2Cl_2$ (40 ml) for 30 s and the mixture was then stirred at r.t. for 30 min. The colour changed from orange to dark red. The solvent was removed under reduced pressure and the residue washed with pentane (2 × 20 ml) to give **5** as a red solid (150 mg, 88%). *Anal.* Calc. for $C_{11}H_{19}Cl_2N_3O_2RuS$ (429): C, 30.77; H, 4.46; N, 9.79. Found: C, 29.56; H, 4.51; N, 9.24%. $^1$H NMR ($CDCl_3$): 8.04 (t, $J = 7.8$, Ar*H*), 7.58 (d, Ar*H*), 4.34 (s, $CH_2$), 2.47 (s, $NMe_2$);

$^{13}C\{^{1}H\}$ ($CDCl_3$): 160.0, 140.5, 121.5 (Ar*C*′s), 72.9 ($CH_2$), 56.2 ($NMe_2$). IR ($CH_2Cl_2$) $\nu$(SO): 1117 (br) $cm^{-1}$.

## 5. Supplementary material

Full details on the X-ray determination of complex **2** are available from the authors.

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