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# Syntheses, structures and reactivity of dinuclear organorutheniumnickel complexes with *N*,*N*'-bis(2-thiobenzylidene)-1,2phenylenediaminato (tsalphen) ligand

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#### Abstract

Treatment of metalloligand [Ni(tsalphen)] (tsalphen = N,N'-bis(2-thiobenzylidene)-1,2phenylenediaminato) with  $[(\eta^6-p\text{-}cymene)\text{RuCl}(\mu\text{-}\text{Cl})]_2$  or  $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$  afforded cationic "Ni( $\mu$ -S)<sub>2</sub>Ru" bimetallic complexes  $[(\eta^6-p\text{-}cymene)\text{Ru}\{\text{Ni}(\text{tsalphen})\}(\text{MeCN})](\text{OTf})_2$  (1) and  $[\text{CpRu}\{\text{Ni}(\text{tsalphen})\}(\text{PPh}_3)]_2(\text{NiCl}_4)\cdot 4\text{MeOH}$  (2), respectively, which are characterized by singlecrystal X-ray diffraction, and their catalytic activity for acetalation of benzaldehyde in the presence of H<sub>2</sub> was also investigated.

*Keywords:* Ni(μ-S)<sub>2</sub>Ru complex; Heterobimetallic; Metalloligand; Organoruthenium complex; Catalytic activity

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#### 1. Introduction

Bioinspired designs thus have led to new catalytic systems for hydrogen production or uptake that minic all or part of the structure of the Fe–Fe hydrogenase active site in the past decades [1]. Furthermore, dinuclear Ni-Fe complexes with significant catalytic activity for the hydrogen evolution reaction have been reported recently [2]. As a unique molecular catalyst for H<sub>2</sub>/H<sup>+</sup> interconversion, hydrogenases are competitive with platinum metal. As a result, people have paid much attention on the synthesis of a great variety of biomimetic complexes with the aim of both better understanding the catalytic mechanism of native [NiFe] and [NiRu] hydrogenases at the molecular level and developing new electrocatalysts to be used in electrolytic/photosynthetic cells for hydrogen production [3]. Since the active sites of the [NiFe] enzymes consist of dithiolate-linked Ni-Fe center bearing little resemblance to known compounds, quite a few Ni-Fe complexes with the structural characterization have been well documented. Typically, such bimetallic complexes are prepared by the interaction of iron reagents with diaminidithiolates of nickel(II), as these diamini-dithiolate building blocks comprise a fairly large class of complexes [4].

As known, ruthenium can easily accommodate both hard and soft ligands including dihydrogen or hydride. Many ruthenium complexes as well as one diruthenium analogue of the iron-only hydrogenase active site are known to catalytically activate hydrogen [5]. Since Darensbourg showed that  $\{NiN_2S_2\}$ moieties can serve as ligands in the same way as diimines [6], it was tempted to use such moieties to prepare and investigate nickel-ruthenium complexes [7]. Notably, Ogo and his coworkers reported the NiRu-based, H<sub>2</sub>O-coordinated bis( $\mu$ -thiolato)Ni<sup>II</sup>Ru<sup>II</sup> complex [(Ni<sup>II</sup>L)Ru<sup>II</sup>(H<sub>2</sub>O)( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)](NO<sub>3</sub>)<sub>2</sub> (A), which successfully reacted with H<sub>2</sub> in water to give a hydrido bridged bis( $\mu$ -thiolato)Ni<sup>II</sup>Ru<sup>II</sup> complex  $[(Ni^{II}L)(H_2O)(\mu-H)Ru^{II}(\eta^6-C_6Me_6)](NO_3)$  (B), where L = N,N'-dimethyl-N,N'-bis(2mercaptoethyl)-1,3-propanediamine [8]. Afterwards, Ogo group reported several other NiRu-based complexes by altering the organoruthenium moieties, such as the aromatic rings, in order to shed light on the structure-function relationships in this class of catalysts, and to gain more insight into the reaction activity of the dinuclear complexes with H<sub>2</sub> [3b,7b,c]. Herein, we described the employment of metalloligand [Ni(tsalphen)] (Chart 1) to prepare new dinuclear organoruthenium-nickel complexes, with the tetradentate rigid ligand around the nickel ion and the organometallic ligand set of the ruthenium center. The reactivity of the structurally defined complexes towards H<sub>2</sub> was also initially investigated.

#### 2. Experimental

#### 2.1. General

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. Published procedures were followed in the preparation of [Ni(tsalphen)] (tsalphen = N,N'-bis(2-thiobenzylidene)-1,2-phenylenediaminato) [9],  $[(\eta^6-p\text{-}cymene)\text{RuCl}(\mu\text{-}Cl)]_2$  [10], and [CpRu(PPh\_3)\_2Cl] (Cp = cyclopentadienyl) [11]. AgOTf (OTf = OSO\_2CF\_3) was purchased from Alfa Aesar Ltd and used without further purification. NMR spectra were recorded on a Bruker ALX 400 spectrometer operating at 400 and 162 MHz for <sup>1</sup>H and <sup>31</sup>P, respectively. Chemical shifts ( $\delta$ , ppm) were reported with reference to SiMe<sub>4</sub> (<sup>1</sup>H) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with use of pressed KBr pellets and positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. GC-MS experiments were performed on a Shimadzu GC-MS 2010 PLUS instrument.

## 2.2. Preparation of $[(\eta^6-p-cymene)Ru\{Ni(tsalphen)\}(MeCN)](OTf)_2(1)$

To a solution of  $[(\eta^6-p-\text{cymene})\text{RuCl}(\mu-\text{Cl})]_2$  (61.2 mg, 0.10 mmol) in methanol (5 mL) was added a solution of AgOTf (102.4 mg, 0.40 mmol) in tetrahydrofuran (THF) (3 mL), and then the mixture was stirred for 20 min at room temperature. The red filtrate was added to the solution of [Ni(tsalphen)] (63.6 mg, 0.20 mmol) in THF (10 mL), the resulting orange solution was continuously stirred overnight at room temperature and then concentrated ca. 1 mL. Slow addition of diethyl ether gave an orange precipitate, which was recrystallized from acetonitrile/diethyl ether. Yield: 58 mg, 83% (based on Ru). Single crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  1.17 (d, *J* = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.21 (s, 3H, ArCH<sub>3</sub>), 2.88 (sept, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.27 (d, *J* = 6.4 Hz, 4H, p*i*PrC<sub>6</sub>H<sub>4</sub>Me), 6.68 (d, *J* = 6.4 Hz, 4H, p-*i*PrC<sub>6</sub>H<sub>4</sub>Me), 6.98-7.08 (m, 2H, ArH), 7.18-7.23 (m, 2H, ArH), 7.30-7.38 (m, 2H, ArH), 7.45-7.56 (m, 2H, ArH), 7.78-7.83 (m, 4H, ArH), 8.90 (s, 2H, N=CH). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>): 19.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.6 (ArCH<sub>3</sub>), 31.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 81.0 (cymene), 81.8 (cymene), 97.2 (cymene), 101.7 (cymene), 118.3 (Ar), 124.6 (Ar), 126.0 (Ar), 129.5 (Ar), 132.8 (Ar), 133.6 (Ar), 134.9 (Ar), 135.5 (Ar), 140.6 (Ar), 168.3 (N=CH). IR (KBr disc, cm<sup>-1</sup>):  $v_{C=N}$  2373(s),  $v_{C=N}$ 

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1603(m). FAB-MS (MeCN): m/z 681.5 [ $(\eta^6-p-\text{cymene})\text{Ru}\{\text{Ni}(\text{tsalphen})\}(\text{MeCN})]^+$ , 640.4 [ $(\eta^6-p-\text{cymene})\text{Ru}\{\text{Ni}(\text{tsalphen})\}]^+$ . Anal. Calc. for C<sub>34</sub>H<sub>31</sub>N<sub>3</sub>O<sub>6</sub>F<sub>6</sub>S<sub>4</sub>NiRu: C, 41.68; H, 3.20; N, 4.29. Found: C, 41.45; H, 3.17; N, 4.22.

#### 2.3. Preparation of $[CpRu{Ni(tsalphen)}(PPh_3)]_2(NiCl_4) \cdot 4MeOH(2)$

A mixture of [Ni(tsalphen)] (81.0 mg, 0.30 mmol) and [CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl] (72.6 mg, 0.15 mmol) in acetonitrile (15 mL) was heated at reflux overnight, during which there was a color change from dark red to dark brown. The solvent was removed in *vacuo*, and the residue was washed with hexane and diethyl ether. Recrystallization from acetonitrile/methanol/diethyl ether afforded black block-shaped crystals of [CpRu{Ni(tsalphen)}(PPh<sub>3</sub>)]<sub>2</sub>(NiCl<sub>4</sub>)·4MeOH (**2**) in a week. Yield: 85 mg, 74% (based on Ru). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  5.61 (s, 5H, Cp), 6.95-7.83 (m, 27H, Ar*H*), 8.87 (s, 2H, N=C*H*). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  51.9. <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>): 78.7 (Cp), 118.9 (Ar), 125.3 (Ar), 126.7 (Ar), 130.0 (Ar), 130.5 (Ar), 133.8 (Ar), 134.0 (Ar), 134.7 (Ar), 136.0 (Ar), 136.9 (Ar), 139.2 (Ar), 142.1 (Ar), 170.1 (N=CH). IR (KBr disc, cm<sup>-1</sup>): *v*<sub>C=N</sub> 1600 (m). FAB-MS (MeCN): *m/z* 831.6 [CpRu{Ni(tsalphen)}(PPh<sub>3</sub>)]<sup>+</sup>, 569.3 [CpRu{Ni(tsalphen)}]<sup>+</sup>. *Anal.* Calc. for C<sub>86</sub>H<sub>64</sub>N<sub>4</sub>Cl<sub>4</sub>P<sub>2</sub>S<sub>4</sub>Ni<sub>3</sub>Ru<sub>2</sub>·4(CH<sub>4</sub>O): C, 54.27; H, 4.05; N, 2.81. Found: C, 54.13; H, 4.11; N, 2.85.

#### 2.4. X-ray crystallography

A summary of crystallographic data and experimental details for complexes **1** and **2** are listed in Table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K. The data was corrected for absorption using the program SADABS [12]. Structures were solved by the direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software package [13]. All non-hydrogen atoms were refined anisotropically except for O3S, O1S and C1S atoms of the solvent molecules due to disorder. Hydrogen atoms in the phenyl and other organic moieties were treated as idealized contributions ( $C_{sp3}$ -H = 0.96 and  $C_{sp2}$ -H = 0.93 Å). One methanol solvent molecule in **2** was refined without hydrogen atoms.

2.5. Typical procedure for acetalation of benzaldehyde with ethanol in the presence of NiRu complexes and H<sub>2</sub>

The catalyst solution was prepared by dissolving complex **1** or **2** (0.005 mmol) in acetonitrile (60 mL). Under 1 atm hydrogen atmosphere, a mixture of aldehyde (2.0 mmol), 6 mL of the catalyst solution (0.0005 mmol), and ethanol (12 mL) was stirred at room temperature for four hours. After the reaction was complete, the reaction mixture was concentrated under reduced pressure and subjected to elimination of catalyst by silica gel column chromatography using ethyl acetate/n-hexane (v:v = 1:5) mixed solvents as eluent to afford the product, which was identified through GC-MS analysis.

#### 3. Results and discussion

The metalloligand [Ni(tsalphen)] was prepared by an alternative method involving four synthetic steps starting from 2-bromobenzaldehyde. To our best knowledge, the reported [NiN<sub>2</sub>S<sub>2</sub>Ru] complexes usually comprise two kinds of flexible ligands, *i.e.* N,N'-dimethyl-N,N'-bis(2-mercaptoethyl)-1,3-propanediamine and 1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane [3a,8]. However, the rigid and conjugate [Ni(tsalphen)] has attracted less attention. The [ $(\eta^6$ -p-cymene)Ru(MeOH)\_3](OTf)<sub>2</sub> may be prepared *in situ* by the dechlorination of [ $\eta^6$ -p-cymene)RuCl( $\mu$ -Cl)]<sub>2</sub> in the prescence of AgOTf in methanol solution. Treatment of a THF solution of [Ni(tsalphen)] with [ $(\eta^6$ -p-cymene)-Ru(MeOH)\_3](OTf)<sub>2</sub> at room temperature furnished orange [ $(\eta^6$ -p-cymene)Ru{Ni(tsalphen)}-(MeCN)](OTf)<sub>2</sub> (1) in a relatively high yield. The cationic complex 1 is air-stable in the solid state but easily oxygenates when exposed to air in solution for a couple of hours. The phosphine ligands in [CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl] are known to be labile, and this encouraged us to carry on the reaction of [Ni(tsalphen)] and [CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl], which afforded the PPh<sub>3</sub> adduct [CpRu{Ni(tsalphen)}-(PPh<sub>3</sub>)]<sub>2</sub>(NiCl<sub>4</sub>)-4MeOH (**2**), isolated as black crystals (Scheme 1). By the comparison of complex **1**, complex **2** is relatively air-stable both in solution and in the solid state.

The IR spectra of complexes **1** and **2** clearly show medium bands of  $v_{C=N}$  in metalloligand moiety [Ni(tsalphen)] at 1603 and 1600 cm<sup>-1</sup>, respectively, which red shifted about 10 cm<sup>-1</sup> compared with that in free [Ni(tsalphen)] (1590 cm<sup>-1</sup>) [9c]. The stretching vibration of the C=N of CH<sub>3</sub>CN was observed in the absorption band at 2373 cm<sup>-1</sup>, which was similar to those of CH<sub>3</sub>CN-coordinated Ru complexes [(HMB)Ru(dppf)(CH<sub>3</sub>CN)](PF<sub>6</sub>)<sub>2</sub> (HMB =  $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>, dppf = 1,1'-bis(diphenylphosphino)ferrocene, 2363 cm<sup>-1</sup>) and [(HMB)Ru(CH<sub>3</sub>CN)<sub>2</sub>Cl](PF<sub>6</sub>) (2359 cm<sup>-1</sup>) [14]. The <sup>1</sup>H NMR spectra of complexes **1** and **2** both show a singlet for the *CH*=N group proton at around 8.90 ppm. The <sup>31</sup>P NMR spectrum of complex **2** displays PPh<sub>3</sub> signal at 51.9 ppm as a singlet, comparable to that in the related complex [CpRu(PPh<sub>3</sub>)S<sub>2</sub>CNSi<sup>*i*</sup>Pr<sub>3</sub>(1-Naphth)] (53.7 ppm) [15]. The positive ion FAB mass spectra of **1** and **2** display the expected peaks which corresponded to the cation ions ([( $\eta^6$ -*p*-cymene)Ru-{Ni(tsalphen)}(MeCN)]<sup>+</sup> or [CpRu{Ni(tsalphen)}(PPh<sub>3</sub>)]<sup>+</sup>, and [( $\eta^6$ -*p*-cymene)Ru{Ni(tsalphen)}]<sup>+</sup> or [CpRu{Ni(tsalphen)}]<sup>+</sup> with the characteristic isotopic distribution patterns.

molecular structures of  $[(\eta^6-p-\text{cymene})\text{Ru}\{\text{Ni}(\text{tsalphen})\}(\text{MeCN})](\text{OTf})_2$  (1) and The  $[CpRu{Ni(tsalphen)}(PPh_3)]_2(NiCl_4) \cdot 4MeOH$  (2) have been established by single crystal X-ray diffraction analysis. Complexes 1 and 2 crystallize in monoclinic  $P2_1/c$  and triclinic  $P\overline{1}$  space groups, respectively. The structures of cationic part  $[(\eta^6 - p - \text{cymene})\text{Ru}\{\text{Ni}(\text{tsalphen})\}(\text{MeCN})]^{2+}$  in **1** and  $[CpRu{Ni(tsalphen)}(PPh_3)]^+$  in 2 are depicted in Figs. 1 and 2, respectively. The structures of both 1 and 2 contain a NiS<sub>2</sub>Ru butterfly core, in which nickel atom and ruthenium atom are located in wing, joined by a pair of bidentate thiolato ligands as the body of the butterfly. The nickel atom adopts a square planar geometry with the tetradentate ligand tsalphen, the bond angles of N(1)-Ni(1)-S(1) and N(2)-Ni(1)-S(2) in 1 are  $176.36(10)^{\circ}$  and  $177.59(10)^{\circ}$ , respectively. The bond angles of N(2)-Ni(1)-S(1) and N(1)-Ni(1)-S(2) in 2 are 177.80(8)° and 176.49(6)°, respectively, almost the same to those in 1. The ruthenium atoms in 1 and 2 both adopt a distorted-octahedral coordination, which is surrounded by one aromatic ring, one metalloligand [Ni(tsalphen)], and one acetonitrile/triphenylphosphine ligand. The Ni–S–Ru angles  $\{84.41(4) \text{ and } 84.39(4)^\circ\}$  of 1 are significantly larger than those of 2  $\{77.89(3) \text{ and } 77.06(3)^\circ\}$ . Due to the larger angles, the distance {3.0760(6) Å} between Ni and Ru in 1 is obviously longer than that in 2 {2.8828(7) Å}, possibly indicating triphenylphosphine coordinated ruthenium species in complex 2 being more stable. In the hydrido-bridged Ni( $\mu$ -H)( $\mu$ -S)<sub>2</sub>Ru complex [(Ni<sup>II</sup>L)(H<sub>2</sub>O)( $\mu$ -H)Ru<sup>II</sup>( $\eta^{6}$ -C<sub>6</sub>Me<sub>6</sub>)](NO<sub>3</sub>) (L = N,N'dimethyl-N,N'-bis(2-mercaptoethyl)-1,3-propanediamine), the Ni…Ru distance is 2.739(3) Å [8]. The ruthenium center in 1 features an CH<sub>3</sub>CN ligand with a Ru–N–C angle of 174.0(4)° and Ru–N distance of 2.082(4) Å, which are normally compared with other bimetallic [Ni( $\mu$ -S)Ru] complexes [Ni<sup>II</sup>( $\mu$ - $SR_2Ru^{II}(CH_3CN)(\eta^6-C_6Me_6)](NO_3)_2$  [( $\mu$ -SR)<sub>2</sub> = N,N'-dimethyl-N,N'-bis(2-mercaptoethyl)-1,3propanediamine, 165.5(2)°, 2.059(2) Å] [7a] and [Cp\*Ru(Ni(bme\*-daco))(NCMe)]OTf (Cp\* = pentamethylcyclodiene,  $bme^*-daco = [1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane],$ 172.2(3)°, 2.051(4) Å) [3a]. The ruthenium center in 2 features a triphenylphosphine ligand with a Ru–P bond length of 2.3311(10) Å, similar to that in related ruthenium(II) complex  $[CpRu(PPh_3)S_2CNSi^iPr_3(1-Naphth)]$  (2.269(2) Å) [15]. The S–Ru–S bond angles in **1** and **2** are 71.21(3)° and 71.77(3)°, respectively, which are in good agreement with those in other reported  $[NiN_2S_2Ru]$  complexes (71.21–75.71°) [3a,8].

As known, Ogo reported that  $[(Ni^{II}L)(H_2O)(\mu-H)Ru^{II}(\eta^6-C_6Me_6)]^+$  with a bridging hydrido ligand could be isolated from the heterolytic cleavage of H<sub>2</sub> by a dinuclear NiRu aqua complex  $[(Ni^{II}L)(H_2O)Ru^{II}(\eta^6-C_6Me_6)]^{2+}$  (L = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine) in water [8]. Complex **2** was tested as the catalyst in the reaction of benzaldehyde and ethanol under dihydrogen atmosphere. Through analysis of GC-MS spectra (see Fig. 3) and comparison with standard compounds, the retention times of 2.171 and 3.242 min correspond to molecular weight of 106 and 180 g·mol<sup>-1</sup>, which in turn correspond to molecular formula of C<sub>7</sub>H<sub>6</sub>O and C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>, respectively. As a result, the species are supposed to be benzaldehyde (C<sub>6</sub>H<sub>5</sub>CHO) and benzaldehyde diethyl acetal (C<sub>6</sub>H<sub>5</sub>CH(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), respectively, based on the designed reaction. This indicates that acetalation of benzaldehyde took place in the presence of dihydrogen and dinuclear organoruthenium-nickel complex **2** in ethanol solvent. The acetalation reaction usually proceeds with H<sup>+</sup> as the catalyst. Controlled reaction without dihydrogen did not give the acetal compound, suggesting dihydrogen being the source of H<sup>+</sup>. PH measurements were performed on the reaction process, which showed that the pH of the solution decreased (from pH 6.5 to pH 5.1), indicating the heterolytic H<sub>2</sub> cleavage [8,16]. However, we did not isolate the expected metal hydride complexes after much effort.

It could be seen from Fig. 3 that the conversion of such acetalation reaction was not high. The impact of temperature, reaction time and the amount of catalyst was systematically investigated (Table 2). When the temperature increased from 0 °C to 40 °C, the conversion of benzaldehyde increased from 1.72% to 14.73%, suggesting the higher temperature benefits the reaction. However, when the temperature is 60 °C, no obvious increase of the conversion was achieved (entry 13). The reaction time also had influence on the reaction. For example, when the reaction was carried at 40 °C, the conversion was 14.37% after 1h, while it reached 25.21% after 5 h, though more reaction time led to little increase (entry 12). As expected, the conversion increased with the increased amount of dinuclear NiRu complex (entry 14). When complex **1** was employed to initiate the reaction, the product benzaldehyde diethyl acetal was also observed. The conversions in this catalytic system are compared to that in other transition metal catalyzed ethanolysis of benzaldehyde [17]. It is noted that the CH<sub>3</sub>CN ligand of

 $[(Ni^{II}L)Ru^{II}(CH_3CN)(\eta^6-C_6Me_6)](NO_3)_2$  could be easily exchanged for H<sub>2</sub>O to give the aqua Ni<sup>II</sup>Ru<sup>II</sup> complex  $[(Ni^{II}L)Ru^{II}(H_2O)(\eta^6-C_6Me_6)](NO_3)_2$ , which converted to be the hydride metal complex after continuous H<sub>2</sub> bubbling [7a]. Possibly heterolytic cleavage of H<sub>2</sub> by the dinuclear NiRu complexes with [Ni(tsalphen)] took place during the acetalation reaction based on the previous research by Ogo, who successfully isolated a paramagnetic dinuclear nickel-ruthenium complex with a bridging hydrido ligand from the heterolytic cleavage of H<sub>2</sub> by a dinuclear NiRu aqua complex [8].

In summary, two thiolate-bridged bimetallic nickel-ruthenium complexes were synthesized and characterized. Isolation of the two nickel-ruthenium complexes suggests that [Ni(tsalphen)] could also be employed as a metalloligand to construct heterobimetallic Ni( $\mu$ -S)<sub>2</sub>Ru complexes. X-Ray diffraction studies establish the Ni…Ru distances in **1** (3.0760(6) Å) and **2** (2.8825(12) Å) are slightly shorter than those in related bimetallic nickel-ruthenium complexes with flexible [N<sub>2</sub>S<sub>2</sub>] ligands [3a, 3b, 7d]. The triphenylphosphine ligand may stabilize the Ni( $\mu$ -S)<sub>2</sub>Ru complex **2**, indicated by its shorter Ni…Ru distance and more stability both in solution and solid state. Complexes **1** and **2** could catalyze acetalation of benzaldehyde with ethanol in the presence of hydrogen.

#### 4. Supplementary material

Crystallographic data for  $[(\eta^6-p\text{-cymene})\text{Ru}\{\text{Ni}(\text{tsalphen})\}(\text{MeCN})](\text{OTf})_2$  (1) and  $[\text{CpRu}\{\text{Ni}(\text{tsalphen})\}(\text{PPh}_3)]_2(\text{NiCl}_4)\cdot 4\text{MeOH}$  (2) been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1578841 and 1578842, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1233-336-033; e-mail: deposit@ccdc.cam.ac.uk].

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Table 1.

Crystallographic data and experimental details for  $[(\eta^6-p-cymene)Ru{Ni(tsalphen)}(MeCN)](OTf)_2(1)$  and  $[CpRu{Ni(tsalphen)}(PPh_3)]_2(NiCl_4)\cdot 4MeOH (2).$ 

complex	1	2
empirical formula	$C_{34}H_{31}N_3O_6F_6S_4NiRu$	$C_{90}H_{80}N_4O_4P_2Cl_4S_4Ni_3Ru_2\\$
formula weight	979.64	1991.83
crystal system	monoclinic	triclinic
<i>a</i> (Å)	11.4100(7)	12.255(2)
<i>b</i> (Å)	20.9518(13)	17.373(3)
<i>c</i> (Å)	16.6336(10)	22.183(3)
$\alpha$ (°)		74.704(3)
$oldsymbol{eta}(^{\circ})$	105.268(1)	74.397(3)
γ(°)		70.397(3)
$V(\text{\AA}^3)$	3836.1(4)	4214.3(13)
space group	$P2_{1}/c$	Pī
Ζ	4	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.696	1.570
temperature (K)	296(2)	296(2)
<i>F</i> (000)	1976	2028
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	1.179	1.326
total refln	23770	26211
independent refln	8745	18452
parameters	497	1011
R <sub>int</sub>	0.0307	0.0516
$R1^{\rm a}, wR2^{\rm b} (I > 2\sigma(I))$	0.0475, 0.1320	0.069 <mark>3</mark> , 0.1572
R1, wR2 (all data)	0.0707, 0.1492	0.17 <mark>37</mark> , 0.20 <mark>32</mark>
GoF <sup>c</sup>	1.065	0.935

<sup>a</sup>  $R1 = ||F_{o}| - |F_{c}||/|F_{o}|.$ <sup>b</sup>  $wR2 = [w(|F_{o}^{2}| - |F_{c}^{2}|)^{2}/w|F_{o}^{2}|^{2}]^{1/2}.$ <sup>c</sup> GoF =  $[w(|F_{o}| - |F_{c}|)^{2}/(N_{obs} - N_{param})]^{1/2}.$ 

entry	catalyst	temperature/°C	time/h	conversion/%
1	2	0	1	1.72
2	2	15	1	2.79
3	2	15	2	6.16
4	2	15	3	10.52
5	2	15	4	14.21
6	2	15	5	16.29
7	2	40	1	14.37
8	2	40	2	18.51
9	2	40	3	20.29
10	2	40	4	23.16
11	2	40	5	25.21
12	2	40	10	26.73
13	2	60	5	25.54
14	$2^{b}$	40	5	37.02
15	1	40	5	24.07

Table 2. Acetalization<sup>*a*</sup> of benzaldehyde with ethanol in the presence of Ni-Ru complexes and  $H_2$ .

<sup>*a*</sup> Reactions were monitored by TLC/GC.

<sup>b</sup> The amount of catalyst is 0.001 mmol (twice of that in entry 11).



**Chart 1.** The structures of two  $[NiN_2S_2]$  metalloligands in NiRu complexes.

Scheme 1. Synthesis of two dinuclear organoruthenium-nickel complexes  $[(\eta^6-p-cymene)Ru{Ni(tsalphen)}(MeCN)](OTf)_2$  (1) and  $[CpRu{Ni(tsalphen)}(PPh_3)]_2(NiCl_4)\cdot 4MeOH$  (2). Reagents and conditions: (i)  $[\eta^6-p-cymene)RuCl(\mu-Cl)]_2 / AgOTf / THF$ , r. t.; (ii)  $[CpRu(PPh_3)_2Cl] / MeCN$ , reflux.



Fig. 1. Molecular structure of the cation of  $[(\eta^6-p\text{-}cymene)\text{Ru}\{\text{Ni}(\text{tsalphen})\}(\text{MeCN})](\text{OTf})_2$  1, with thermal ellipsoids drawn at the 40% probability level. Hydrogen atoms and anions are omitted for clarity. Selected bonds (Å) and angles (°): Ru(1)-N(3) 2.082(4), Ru(1)-C(7) 2.173(5), Ru(1)-C(3) 2.183(4), Ru(1)-C(6) 2.201(5), Ru(1)-C(4) 2.207(4), Ru(1)-C(2) 2.208(5), Ru(1)-C(5) 2.221(5), Ru(1)-S(2) 2.4086(10), Ru(1)-S(1) 2.4169(10), Ru(1)-Ni(1) 3.0760(6), Ni(1)-N(2) 1.890(3), Ni(1)-N(1) 1.896(3), Ni(1)-S(1) 2.1529(11), Ni(1)-S(2) 2.1633(11); S(2)-Ru(1)-S(1) 71.21(3), N(2)-Ni(1)-N(1) 85.60(14), S(1)-Ni(1)-S(2) 81.21(4), N(1)-Ni(1)-S(1) 176.36(10), N(2)-Ni(1)-S(2) 177.59(10), Ni(1)-S(1)-Ru(1) 84.41(4), Ni(1)-S(2)-Ru(1) 84.39(4).



**Fig. 2.** Molecular structure of one anion of [CpRu{Ni(tsalphen)}(PPh<sub>3</sub>)]<sub>2</sub>(NiCl<sub>4</sub>)·4MeOH **2**, with thermal ellipsoids drawn at the 40% probability level. Hydrogen atoms, the other cation and the counter anion are omitted for clarity. Selected bonds (Å) and angles (°): Ru(1)-P(1) 2.3311(10), Ru(1)-S(1) 2.4087(8), Ru(1)-S(2) 2.4345(8), Ru(1)-Ni(1) 2.8828(7), Ni(1)-N(1) 1.901(3), Ni(1)-N(2) 1.918(2), Ni(1)-S(1) 2.1678(8), Ni(1)-S(2) 2.1826(10); S(1)-Ru(1)-S(2) 71.77(3), N(1)-Ni(1)-N(2) 85.41(10), S(1)-Ni(1)-S(2) 81.47(4), N(2)-Ni(1)-S(1) 177.80(8), N(1)-Ni(1)-S(2) 176.49(6), Ni(1)-S(1)-Ru(1) 77.89(3), Ni(1)-S(2)-Ru(1) 77.06(3).



Fig. 3. GC-MS analysis of product from reaction of benzaldehyde and ethanol under  $H_2$  atmosphere catalyzed by complex 2, (a) GC; (b) MS.

## For Table of Contents

<u>Synopsis</u>

# Syntheses, structures and reactivity of dinuclear organoruthenium-nickel complexes with *N*,*N*'-bis(2-thiobenzylidene)-1,2-phenylenediaminato (tsalphen) ligand

Ai-Quan Jia, Li-Hua Tang, Xian-Ping Dong, Zhifeng Xin, and Qian-Feng Zhang\*

Two cationic bimetallic organoruthenium-nickel Ni( $\mu$ -S)<sub>2</sub>Ru complexes containing metalloligand [Ni(tsalphen)] have been synthesized and characterized by X-ray crystallography, they could catalyze acetalation of benzaldehyde with ethanol in the presence of H<sub>2</sub>.



# Highlights

- ► Two dinuclear nickel-ruthenium complexes with tsalphen ligand were synthesized.
- ► The Ni( $\mu$ -S)<sub>2</sub>Ru complexes were characterized by single crystal X-ray crystallography.
- They catalyze acetalation of benzaldehyde with ethanol in the presence of  $H_2$ .

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