# Ruthenium thiocarbonyl and phosphoniodithiocarboxylate complexes with an oxygen tripod ligand

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## Abstract

Treatment of $[Ru(CO)_2Cl_2]_x$ with $NaL_{OEt}$ ($L_{OEt}^- = [Co(\eta^5-C_5H_5)\{P(O)(OEt)_2\}_3]^-$) afforded $[L_{OEt}Ru(CO)_2Cl]$ (**1**), which reacted with $AgBF_4$ in acetone–$H_2O$ to give $[L_{OEt}Ru(CO)_2(H_2O)][BF_4]$ (**2**). Reaction of $[L_{OEt}Ru(CH=CHPh)(CO)(PPh_3)]$ with HCl gave $[L_{OEt}RuCl(CO)(PPh_3)]$ (**3**), which has been characterized by X-ray crystallography. The Ru–C, Ru–P, Ru–Cl and average Ru–O distances in **3** are 1.993(7), 2.2811(13), 2.376(2) and 2.137 Å, respectively. Interaction of $[L_{OEt}Ru(PPh_3)_2Cl]$ with $CS_2$ and $PR_3$ in the presence of $[NH_4][PF_6]$ afforded the ruthenium(II) phosphoniodithiocarboxylate species $[L_{OEt}Ru(PPh_3)(\eta^2-S_2CPR_3)][PF_6]$ (R = Ph (**4**) or cyclohexyl (**5**)). Oxidation of **4** with $AgBF_4$ yielded the ruthenium(III) complex $[L_{OEt}Ru(PPh_3)(\eta^2-S_2CPPh_3)][BF_4][PF_6]$ (**6**), which has been characterized by X-ray crystallography. The Ru–P, average Ru–O and average Ru–S distances in **6** are 2.3978(10), 2.078 and 2.2910 Å, respectively. The ruthenium(II) thiocarbonyl complex $[L_{OEt}Ru(CS)Cl(PPh_3)]$ (**7**) was prepared from $NaL_{OEt}$ and $[Ru(CS)Cl_2(PPh_3)_2]_2$. The Ru–Cl, Ru–P, Ru–C and average Ru–O distances in **7** are 2.3681(10), 2.3043(9), 1.823(4), and 2.140 Å, respectively. Treatment of **7** with $AgBF_4$ in acetone–$H_2O$ afforded $[L_{OEt}Ru(CS)(PPh_3)(H_2O)][BF_4]$ (**8**). On the basis of the Ru(III/II) formal potential, CS was found to be a stronger π acid ligand than CO. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Ruthenium; Oxygen tripod ligand; Thiocarbonyl; Phosphoniodithiocarboxylate

## 1. Introduction

The π-donating oxygen tripod ligand $[CpCo\{P(O)(OR)_2\}_3]^-$ ($L_{OR}^-$, R = alkyl) or the Kläui's tripod ligand is of interest due to its ability to stabilize transition metal ions in high oxidation states [1]. $L_{OR}^-$ have also been used as models for facially disposed aquo ligands [2]. There are, however, relatively few studies on the organometallic chemistry of $L_{OR}$–Ru complexes [3,4]. Previously we found that the electron-rich $L_{OEt}$–Ru core is capable of stabilizing a variety of π accepting hydrocarbyl ligands including carbene, vinylidene, allenylidene, vinyl and σ-acetylide [4]. To our knowledge, no ruthenium thiocarbonyl complexes with $L_{OR}$ have been reported. Because of its reactivity toward migratory insertion and nucleophilic attack, thiocarbonyl ligand has been served as model for metal-mediated reactions of carbonyl [5]. For example, Hill et al. reported that the reaction of a Ru(II) thiocarbonyl complex with thiophenolate afforded Ru(II) $\eta^2$-thioester species [6]. As part of our programme to investigate homogeneous catalysis based on ruthenium complexes with oxygen donor ligands, we here describe the synthesis and molecular structures of ruthenium thiocarbonyl and phosphoniodithiocarboxylate complexes with $L_{OEt}^-$.

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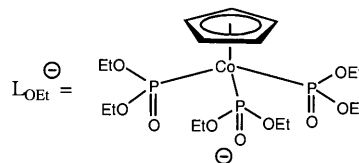
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## 2. Results and discussion

### 2.1. Ruthenium carbonyl complexes

Kläui and coworkers first synthesized [$L_{OEt}$Ru-$(CO)_2$Cl] (**1**) by the reaction of $RuCl_3$ with $NaL_{OEt}$ and CO in ethanol [1]. We found that complex **1** could also be prepared from [$Ru(CO)_2Cl_2$]$_x$ and $NaL_{OEt}$ in DMF, and was purified by column chromatography. The $\nu(C\equiv O)$ for **1** (2044 and 1964 cm$^{-1}$) were found to be lower than those for [$CpRu(CO)_2Cl$] (2059 and 2008 cm$^{-1}$) [7] and [$TpRu(CO)_2Cl$] (Tp = trispyrazolylborate, 2074 and 2012 cm$^{-1}$) [8], consistent the order of donor strength for the 6e ligands $L_{OEt}^- > Cp \approx Tp$ [1]. Treatment of **1** with $AgBF_4$ in boiling acetone–$H_2O$ afforded the aquo complex [$L_{OEt}Ru(CO)_2(OH_2)$][$BF_4$] (**2**), isolated as air-stable yellow crystals. As expected, the IR $\nu(C\equiv O)$ for **2** (2056 and 1988 cm$^{-1}$) are higher than those for **1** due to cationic nature of the complex. An attempt to prepare a Ru(II) hydroxide by treatment of **2** with NaOH [4c] was unsuccessful.

Previously we reported that protonation of [$L_{OEt}Ru(CH=CHPh)(CO)(PPh_3)$] with $HBF_4$ gave a labile Ru(II) $\eta^2$-styrene species, which upon recrystallization from wet $CH_2Cl_2$ yielded [$L_{OEt}Ru$-$(CO)(PPh_3)(H_2O)$]$^+$ [4a]. When [$L_{OEt}Ru(CH=CHPh)$-$(CO)(PPh_3)$] was treated with HCl in ether, the chloride compound [$L_{OEt}Ru(CO)(PPh_3)Cl$] (**3**) was isolated in good yield. Owing to the presence of the electron-releasing $PPh_3$ ligand, the IR CO $\nu(CO)$ for **3** (1936 cm$^{-1}$) is lower than those for **1**. The structure of **3** has
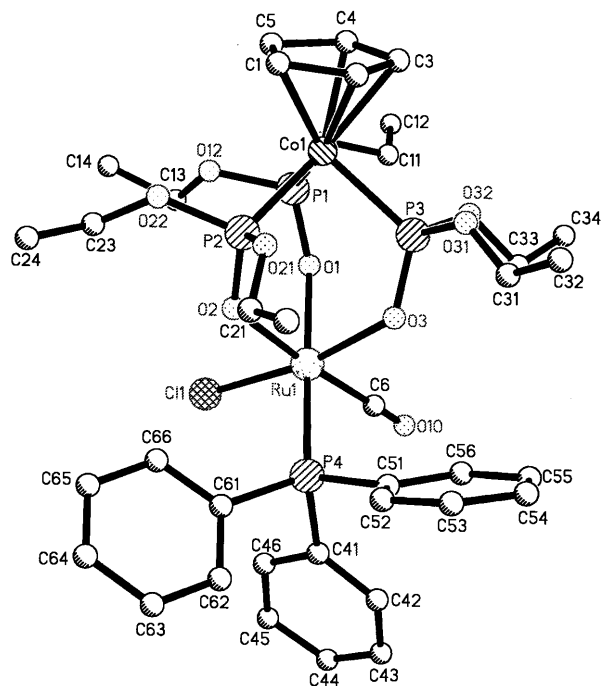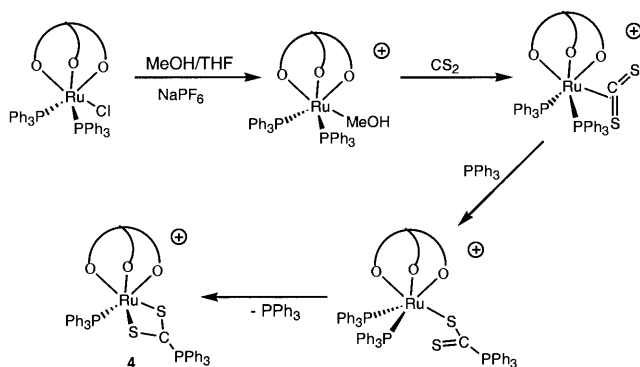
been established by X-ray crystallography. Fig. 1 shows a perspective view of the molecule; selected bond lengths and angles are listed in Table 2. The average Ru–O (2.137 Å) and Ru–Cl (2.376(2) Å) distances are similar to those for [$L_{OEt}Ru(COD)Cl$] (COD = 1,5-cyclooctadiene) [4c]. The Ru–C (1.993(7) Å) and Ru–P (2.2811(13) Å) distances are comparable to those for [$L_{OEt}Ru(PPh_3)(CO)(H_2O)$]$^+$ [4c].

### 2.2. Ruthenium phosphoniodithiocarboxylate complexes

Phosphine-mediated desulfurization of $CS_2$ is a commonly used synthetic route to ruthenium(II) thiocarbonyl complexes such as [$RuCl_2(OH_2)(CS)(PPh_3)_2$] [9]. Thus, in a hope to synthesize ruthenium thiocarbonyl complexes, reaction of [$L_{OEt}Ru(PPh_3)_2Cl$] with $CS_2$ in the presence of $PPh_3$ was attempted. Treatment of [$L_{OEt}Ru(PPh_3)_2Cl$] with $CS_2$ and $PPh_3$ in THF led to isolation of an uncharacterized orange paramagnetic species that did not crystallize. However, when the reaction was carried out in MeOH–THF in the presence of $NaPF_6$, a purple solid characterized as a ruthenium(II) phosphoniodithiocarboxylate complex [$L_{OEt}(PPh_3)Ru(\eta^2\text{-}S_2CPPh_3)$][$PF_6$] (**4**) was isolated. There was no evidence for formation of ruthenium(II) thiocarbonyl or carbon disulfide complexes in the reaction. The choice of solvent is critical for the formation of the Ru phosphoniodithiocarboxylate species obviously because [$L_{OEt}Ru(PPh_3)_2Cl$] is known to undergo chloride dissociation in MeOH [4a]. The $^{31}P\{^1H\}$-NMR spectrum for **4** shows two singlets at $\delta$ 50 and 1.65, which are assigned to $PPh_3$ and $S_2CPPh_3$, respectively. The FAB mass spectrum shows a signal at $m/z$ 1237 attributable to the parent ion ($M^+$–$PF_6$ + 1). It appears that the phosphoniodithiocarboxylate ligand in **4** was formed by addition of $PPh_3$ to coordinated $CS_2$ rather than via $CS_2$ insertion into Ru–$PPh_3$ [10] because reaction of [$L_{OEt}Ru(PPh_3)_2Cl$] with $CS_2$ and $PCy_3$ (Cy = cyclohexyl) under the same conditions afforded [$L_{OEt}Ru(\eta^2\text{-}S_2CPCy_3)(PPh_3)$][$PF_6$] (**5**) only. The $^{31}P$ resonances for the $PPh_3$ and $PCy_3$ in **5** were observed at $\delta$ 53.2 and 18.7, respectively. It may be noted that [($\eta^6$-arene)RuCl($S_2CPR_3$)]$^+$ was formed by the reaction of [($\eta^6$-arene)$RuCl_2$]$_2$ with $S_2CPR_3$ in the presence of $KPF_6$ [11] while $CS_2$ insertion into the Ru–P$^i$Pr$_3$ bond was suggested to be involved in the formation of [$RuCl_2(CO)(P^iPr_3)(\eta^2\text{-}S_2CP^iPr_3)$] from [$RuCl_2(CO)$-$(P^iPr_3)_2$] and $CS_2$ [12]. The proposed mechanism for formation of **4** is shown in Scheme 1. Chloride dissociation of [$L_{OEt}Ru(PPh_3)_2Cl$] in MeOH gave cationic [$L_{OEt}Ru(PPh_3)_2(MeOH)$]$^+$, which reacted with $CS_2$ to give a Ru(II)–$CS_2$ intermediate. Nucleophilic attack at the coordinated $CS_2$ by $PPh_3$ followed by phosphine dissociation yielded **4**.
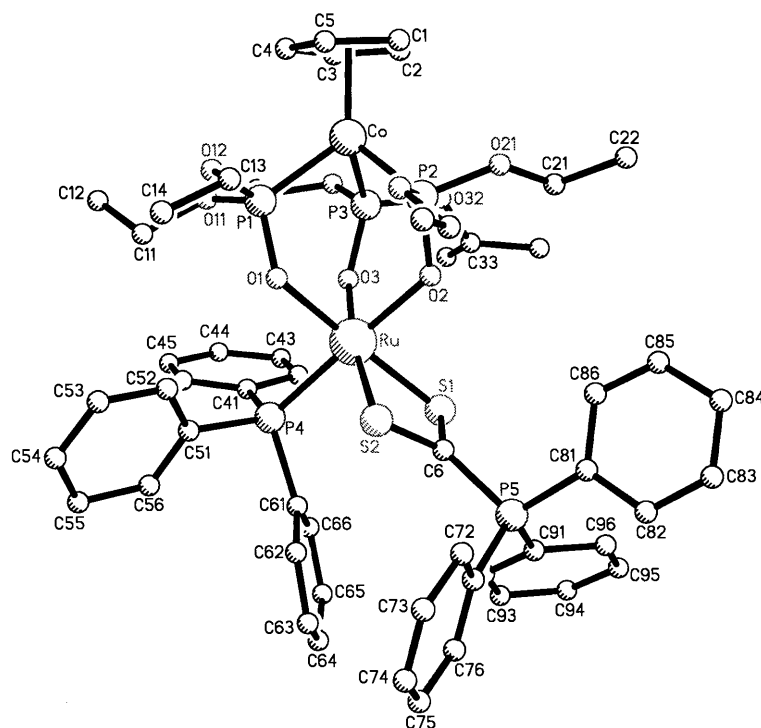


Fig. 1. Perspective view of [$L_{OEt}Ru(CO)(PPh_3)Cl$] (**3**).

Scheme 1.

Oxidation of **4** with AgBF$_4$ in CH$_2$Cl$_2$ afforded the ruthenium(III) complex [L$_{OEt}$Ru($\eta^2$-S$_2$CPPh$_3$)(PPh$_3$)]-[PF$_6$][BF$_4$] (**6**), isolated as purple crystals. The measured magnetic moment of 1.8 $\mu_B$ for **6** is consistent with the Ru$^{III}$ formulation. The structure of **6** has been unambiguously established by X-ray crystallography. Fig. 2 shows a perspective view of the di-cation [L$_{OEt}$Ru($\eta^2$-S$_2$CPPh$_3$)(PPh$_3$)]$^{2+}$; selected bond lengths and angles are listed in Table 3. To our knowledge, complex **6** is the first phosphoniodithiocarboxylate complex of Ru(III). The S$_2$CPPh$_3$ ligand binds to Ru in a *S,S'*-$\eta^2$ fashion, consistent with the formulation of a 4e ligand [10]. The average Ru–S distance in **6** of 2.291 Å is shorter than those in [Ru(S$_2$CNEt$_2$)$_3$] (average 2.38 Å) [13] and [RuCl$_2$(CO)(P$^i$Pr$_3$)($\eta^2$-S$_2$CP$^i$Pr$_3$)] (2.413 Å)

[12]. The average C–S bond distance (1.687 Å) and P–C distance (1.813(3) Å) are similar to those for S$_2$CPEt$_3$ (1.69 and 1.79(3) Å, respectively) [14], consistent with the zwitterionic form of the S$_2$CPPh$_3$ ligand. The Ru–P and average Ru–O distances in **6** are comparable to those for [L$_{OEt}$Ru(PPh$_3$)$_2$Cl]$^+$ [4a]. The Ru$^{III}$–P distance (2.3978(10) Å) in **6** is longer than the Ru$^{II}$–P bond in **3** apparently due to strong $\pi$ bonding between Ru(II) and PPh$_3$. A similar result has also been observed for the [L$_{OEt}$Ru(PPh$_3$)$_2$Cl]$^{0/+}$ system [4a].

### 2.3. Ruthenium thiocarbonyl complexes

The Ru(II) thiocarbonyl complex [L$_{OEt}$Ru(CS)(PPh$_3$)Cl] (**7**) was successfully synthesized by the reaction of [Ru(CS)Cl$_2$(PPh$_3$)$_2$]$_2$ with NaL$_{OEt}$ in boiling THF, isolated as air stable red crystals. The solid-state structure of **7** has been established by X-ray crystallography. Fig. 3 shows a perspective view of **7**; selected bond lengths and angles are collected in Table 4. The Ru–P, Ru–C and Ru–Cl distances of 2.3043(9), 1.823(4) and 2.3681(10) Å are similar to those for **3**. The Ru–C–S linkage for **7** is roughly linear (178.0(2)°). The Ru–C distance in **7** is short and is similar to that in [($\eta^5$-C$_5$Me$_5$)Ru(CS)(PPh$_2$R)$_2$][BPh$_4$] (R = 1,3-dioxan-2-ylmethyl, 1.832(4) Å) [15], indicative of multiple bond character of the Ru–C bond. For **7**, the Ru–O(*trans* to C) distance (2.174(2) Å) is obviously longer than the Ru–O(*cis* to C) (2.141(2) and 2.106(2) Å) due to *trans* influence of thiocarbonyl. By contrast, for the carbonyl



Fig. 2. Persective view of the di-cation [L$_{OEt}$Ru($\eta^2$-S$_2$CPPh$_3$)(PPh$_3$)]$^{2+}$.
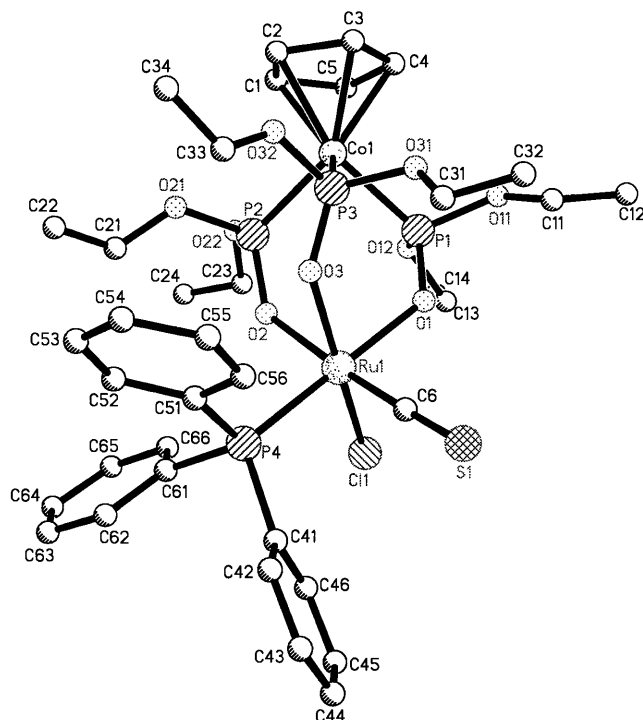
Fig. 3. Perspective view of [L_{OEt}Ru(CS)(PPh_3)Cl] (**7**).

complex **3** the Ru–O(*trans* to C) (2.142(3) Å) is slightly shorter than the Ru–O(*trans* to P) (2.151(3) Å). These findings suggest that CS is a stronger *trans* ligand than CO (see Section 2.4). The IR $\nu$(C≡S) for **7** occurs in a relatively high energy (1296 cm$^{-1}$), indicating that the Ru center is rather electron-deficient (e.g. cf. 1281 cm$^{-1}$ for ([Ru([9]aneS_3)Cl(CS)(PPh_3)][PF_6]) [6], and that the thiocarbonyl ligand may be prone to nucleophilic attack. However reaction of **7** with thiophenol–Et_3N led to formation of a green intractable material. Nor were there any crystalline products isolated from the reactions between **7** and electrophiles such as methyl triflate and [Au(PPh_3)(O_3SCF_3)]. Treatment of **7** with AgBF_4 in boiling acetone–H_2O afforded cationic [L_{OEt}Ru(PPh_3)(CS)(OH_2)][BF_4] (**8**), isolated as yellow crystals. Reaction of **8** with 4-*tert*-butylpyridine ($^t$Bupy) afforded the adduct [L_{OEt}Ru(PPh_3)(CS)($^t$Bupy)][BF_4] (**9**) characterized by NMR spectroscopy.

## 2.4. Electrochemistry

The formal potentials for the Ru–L_{OEt} complexes in CH_2Cl_2 were determined by cyclic voltammetry. The cyclic voltammogram of the carbonyl compound **3** shows a reversible couple at 0.450 V, which was assigned as the Ru(III/II) couple. The Ru(III/II) potential for **3** is more anodic than that for [L_{OEt}Ru(PPh_3)_2Cl] (−0.02 V) [4a] but less than that for the thiocarbonyl compound **7** (0.520 V), implying the order of $\pi$ acidity CS > CO > PPh_3. No couples were found for the dicar-

bonyl compound **1** because the Ru(II) state is strongly stabilized by the two carbonyl ligands. Compound **4** exhibits a reversible couple at 0.180 V that was assigned as the Ru(III/II) couple. The Ru(III/II) couple for the tricyclohexyl analogue **5** occurs at a slightly less positive potential (0.153 V) because of the electron-releasing cyclohexyl groups. The Ru(III/II) potentials for these phosphoniodithiocarboxylate complexes are more anodic than that for [L_{OEt}Ru(PPh_3)_2Cl], indicating that S_2CPR_3 are not particularly strong donor ligands.

## 2.5. Summary

We have isolated the first ruthenium thiocarbonyl and phosphoniodithiocarboxylate complexes containing the oxygen tripod ligand L$^-_{OEt}$. On the basis of X-ray diffraction data and Ru(III/II) redox potentials, it was found that thiocarbonyl is a stronger $\pi$ acid ligand than carbonyl with respect to Ru(II). Oxidation of [L_{OEt}Ru(PPh_3)($\eta^2$-S_2CPPh_3)]$^+$ with Ag(I) afforded stable [L_{OEt}Ru(PPh_3)($\eta^2$-S_2CPPh_3)]$^{2+}$.

## 3. Experimental

### 3.1. General information

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. Infrared spectra (Nujol) were recorded on a Perkin–Elmer 16 PC FT-IR spectrophotometer and mass spectra on a Finnigan TSQ 7000 spectrometer. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for $^1$H and $^{31}$P, respectively. Chemical shifts ($\delta$, ppm) were reported with reference to SiMe_4 ($^1$H) and H_3PO_4 ($^{31}$P). The magnetic moment for complex **7** in the solid state was determined by a Sherwood magnetic susceptibility balance at room temperature. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat. The working and reference electrodes were glassy carbon and Ag–AgNO_3 (0.1 M in acetonitrile), respectively, and the scan rate was 100 mV s$^{-1}$. Formal potentials ($E°$) were measured in CH_2Cl_2 solutions with 0.1 M [N$^n$Bu_4][PF_6] as supporting electrolyte and reported with reference to the ferrocenium–ferrocene couple. Elemental analyses were performed by Medac Ltd, Surrey, UK.

The ligand NaL_{OEt} was prepared according to the Kläui's procedure [16]. The compounds [L_{OEt}Ru(CH=CHPh)(CO)(PPh_3)], [L_{OEt}Ru(PPh_3)_2Cl] [4a], [Ru(CO)_2Cl_2]_x [17] and [RuCl_2(CS)(PPh_3)_2]_2 [18] were prepared according to the literature methods.

## 3.2. [L$_{OEt}$Ru(CO)$_2$Cl] (1)

A mixture of [Ru(CO)$_2$Cl$_2$]$_x$ (0.08 g, 0.35 mmol) and NaL$_{OEt}$ (0.02 g, 0.36 mmol) in DMF (50 ml) was heated at reflux overnight. The solvent was removed in vacuo and the residue extracted with CH$_2$Cl$_2$. The filtrate was concentrated and loaded onto a silica gel column. The product was eluted with hexane–CH$_2$Cl$_2$ (5:1) as a yellow band. Recrystallization from hexane–Et$_2$O afforded yellow crystals. Yield: 0.1 g (40%). Anal. Calc. for C$_{19}$H$_{35}$ClCoO$_{11}$P$_3$Ru: C, 31.34; H, 4.61. Found: C, 31.45; H, 4.92%. $^1$H-NMR (CDCl$_3$): $\delta$ 1.26 (overlapping t, 12H, C$H_3$), 1.31 (t, 6H, C$H_3$), 3.90–4.04 (m, 4H, C$H_2$), 4.12–4.27 (m, 8H, C$H_2$), 5.01 (s, 5H, C$_5$H$_5$). $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ 113.3 (m, L$_{OEt}$). IR (cm$^{-1}$): 2044, 1964 [$\nu$(CO)].

## 3.3. [L$_{OEt}$Ru(CO)$_2$(H$_2$O)][BF$_4$] (2)

To a solution of 1 (0.15 g, 0.2 mmol) in acetone–H$_2$O (40 ml, 1:1) was added AgBF$_4$ (0.004 g, 0.2 mmol) and the mixture was heated at reflux for 1 h. The AgCl precipitate was filtered off and the mixture was evaporated to dryness. Recrystallization from CH$_2$Cl$_2$–hexane afforded yellow crystals. Yield: 0.05 g (60%). Anal. Calc. for C$_{19}$H$_{37}$BCoF$_4$O$_{12}$P$_3$Ru: C, 28.61; H, 4.64. Found: C, 27.84; H, 4.81%. $^1$H-NMR (CDCl$_3$): $\delta$ 1.27 (t, 6H, C$H_3$), 1.31 (t, 6H, C$H_3$), 1.33 (t, 6H, C$H_3$), 3.93–4.03 (m, 4H, C$H_2$), 4.14–4.22 (m, 8H, C$H_2$), 5.10 (s, 5H, C$_5$H$_5$); the resonance signal for the aqua ligand was not observed. $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ 115.8 (m, L$_{OEt}$). IR (cm$^{-1}$): 2056, 1988 [$\nu$(CO)].

## 3.4. [L$_{OEt}$Ru(CO)(PPh$_3$)Cl] (3)

To a solution of [L$_{oEt}$Ru(CO)(PPh$_3$)(CH=CHPh)] (0.08 g, 0.083 mmol) in CH$_2$Cl$_2$ was added slowly HCl (11.3 ml of 1 M solution in Et$_2$O, 0.088 mmol) at −78°C. The yellow solution changed to orange and then yellow after warming to room temperature. The volatiles were removed and the residue was washed with hexane. The residue was extracted with ether (3 × 10 ml) and the solution was recrystallized from ether to give yellow crystals from which suitable crystal was selected for X-ray crystallography. Yield: 0.045 g (56%). Anal. Calc. for C$_{36}$H$_{50}$ClCoO$_{10}$P$_4$Ru: C, 44.94; H, 5.24. Found: C, 45.14; H, 5.34%. $^1$H-NMR (CDCl$_3$): $\delta$ 0.99 (t, 6H, C$H_3$), 1.36–1.48 (m, 12H, C$H_3$), 3.16–3.22 (m, 4H, OC$H_2$), 4.12–4.56 (m, 8H, OC$H_2$), 5.03 (s, 5H, C$_5$H$_5$), 7.37–7.80 (m, 15H, PPh$_3$). $^{31}$P{$^1$H}, $\delta$ 52.5 (s, PPh$_3$), 118.0 (m, L$_{OEt}$). IR (cm$^{-1}$): 1936 [$\nu$(CO)]. MS (FAB): $m/z$ 962 (M$^+$ + 1), 927 (M$^+$ − Cl + 1). $E°$ (CH$_2$Cl$_2$) = + 0.450 V [Ru(III/II)].

## 3.5. [L$_{OEt}$Ru($\eta^2$-S$_2$CPPh$_3$)(PPh$_3$)][PF$_6$] (4)

To a solution of 1 (0.09 g, 0.075 mmol), NaPF$_6$ (0.0015 g, 0.088 mmol) and PPh$_3$ (0.025 g, 0.114 mmol) in THF–MeOH (20 ml, 1:4) was added CS$_2$ (0.5 ml) and the reaction mixture was stirred at room temperature for 1 day, during which the color changed from orange to purple. The volatiles were removed and the residue was recrystallized from CH$_2$Cl$_2$–hexane to give purple crystals. Yield: 0.066 g (64%). Anal. Calc. for C$_{54}$H$_{65}$CoF$_6$O$_9$P$_6$RuS$_2$: C, 46.92; H, 4.71. Found: C, 46.10; H, 4.90%. $^1$H-NMR (CDCl$_3$): $\delta$ 0.87 (t, 6H, C$H_3$), 1.25 (t, 6H, C$H_3$), 1.27 (t, 6H, CH$_3$), 3.21–3.51 (m, 4H, OC$H_2$), 4.0–4.1 (m, 8H, OC$H_2$), 4.93 (s, 5H, C$_5$H$_5$), 7.14–7.59 (m, 30H, PPh$_3$). $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ 50.0 (s, PPh$_3$), 1.65 (s, S$_2$CPPh$_3$), 111.2 (m, L$_{OEt}$). MS (FAB): $m/z$ 1237 (M$^+$ − PF$_6$ + 1). $E°$(CH$_2$Cl$_2$) = + 0.180 V [Ru(III/II)].

## 3.6. [L$_{OEt}$Ru($\eta^2$-S$_2$CPCy$_3$)(PPh$_3$)][PF$_6$] (5)

To a solution of 1 (0.08 g, 0.067 mmol), NaPF$_6$ (0.015 g, 0.088 mmol) and tricyclohexyl phosphine (0.025 g, 0.89 mmol) in THF–MeOH (20 ml, 1:4) was added CS$_2$ (0.5 ml) and the reaction mixture was stirred at room temperature for 1 day, during which the colour changed from orange to purple. The volatiles were removed and the residue was recrystallized from CH$_2$Cl$_2$–hexane to give purple crystals. Yield: 0.047 g (50%). Anal. Calc. for C$_{54}$H$_{83}$CoF$_6$O$_9$P$_6$RuS$_2$: C, 46.32; H, 5.93. Found: C, 45.10; H, 6.02%. $^1$H-NMR (CDCl$_3$): $\delta$ 1.00 (t, 6H, C$H_3$), 1.35 (t, 6H, C$H_3$), 1.38 (t, 6H, C$H_3$), 1.40–1.90 (m, 30H, Cy protons), 2.50–2.58 (m, 3H, C$H$), 3.30–3.44 (m, 4H, OC$H_2$), 4.08–4.17 (m, 8H, OC$H_2$), 5.01 (s, 5H, C$_5$H$_5$), 7.31–7.58 (m, 15H, PPh$_3$). $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ 53.2 (s, PPh$_3$), 110.4 (m, L$_{OEt}$), 18.7 (PCy$_3$). MS (FAB): $m/z$ 1255 (M$^+$ − PF$_6$ + 1). $E°$(CH$_2$Cl$_2$) = + 0.153 V [Ru(III/II)].

## 3.7. [L$_{OEt}$Ru($\eta^2$-S$_2$CPPh$_3$)(PPh$_3$)][PF$_6$][BF$_4$] (6)

To a CH$_2$Cl$_2$ solution of 4 (0.05 g, 0.036 mmol) was added AgBF$_4$ (0.015 g, 0.057 mmol) and the reaction mixture was stirred at room temperature for 1 h and filtered. Recrystallization from CH$_2$Cl$_2$–hexane afforded purple crystals, which were suitable for X-ray analysis. Yield: 0.016 g (30%). Anal. Calc. for C$_{54}$H$_{65}$BCoF$_{10}$O$_9$P$_6$RuS$_2$: C, 44.14; H, 4.43. Found: C, 44.80; H, 4.81%. $\mu_{eff}$ = 1.8 $\mu_B$.

## 3.8. [L$_{OEt}$Ru(CS)(PPh$_3$)Cl] (7)

A mixture of [RuCl$_2$(CS)(PPh$_3$)$_2$]$_2$ (0.19 g, 0.27 mmol) and NaL$_{OEt}$ (0.15 g, 0.269 mmol) in THF (25

Table 1
Crystallographic data and experimental details for [L$_{OEt}$Ru(CO)(PPh$_3$)Cl] (**3**), [L$_{OEt}$Ru($\eta^2$-S$_2$CPPh$_3$)(PPh$_3$)][BF$_4$][PF$_6$] (**6**), and [L$_{OEt}$Ru(PPh$_3$)(CS)Cl] (**7**)

| Compound | **3** | **6** | **7** |
|---|---|---|---|
| Empirical formula | C$_{36}$H$_{50}$ClCoO$_{10}$P$_4$Ru | C$_{54}$H$_{65}$BCoF$_{10}$O$_9$P$_6$RuS$_2$ | C$_{36}$H$_{50}$ClCoO$_9$P$_4$RuS |
| Formula weight | 962.09 | 1468.81 | 978.15 |
| Color; habit | Red; block | Brown; block | Orange–brown; block |
| $a$ (Å) | 14.0760(10) | 12.579(2) | 14.148(2) |
| $b$ (Å) | 14.8040(10) | 26.416(3) | 15.141(2) |
| $c$ (Å) | 20.729(2) | 19.050(3) | 20.468(3) |
| $\beta$ (°) | 92.640(10) | 91.130(10) | 93.250(10) |
| $U$ (Å$^3$) | 4314.9(6) | 6328.8(16) | 4377.5(11) |
| $Z$ | 4 | 4 | 4 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/n$ (no. 14) |
| $D_{calc}$ (g cm$^{-3}$) | 1.481 | 1.542 | 1.484 |
| $T$ (K) | 293(2) | 293(2) | 293(2) |
| $\mu$ (cm$^{-1}$) | 9.95 | 7.99 | 10.27 |
| Total number of reflections | 8484 | 13350 | 9984 |
| Number of reflections observed ($I>2\sigma(I)$) | 5850 | 10156 | 7515 |
| $R^a$ | 0.0894 | 0.0703 | 0.0644 |
| w$R_2^b$ (all data) | 0.1434 | 0.1390 | 0.1108 |
| Goodness-of-fit | 1.028 | 1.025 | 1.036 |

ml) was heated at reflux overnight. The volatiles were removed in vacuo, and the residue was washed with hexane. Recrystallization from Et$_2$O–hexane afforded orange crystals, which were suitable for X-ray analysis. Yield: 0.14 g (52%). Anal. Calc. for C$_{36}$H$_{50}$-ClCoO$_9$P$_4$RuS: C, 44.17; H, 5.11. Found: C, 44.8; H, 5.08%. $^1$H-NMR (CDCl$_3$): $\delta$ 0.84 (t, 3H, C$H_3$), 0.91 (t, 3H, C$H_3$), 1.27 (t, 3H,C$H_3$), 1.29 (t, 3H, C$H_3$), 1.31 (t, 3H, C$H_3$), 1.34 (t, 3H, C$H_3$), 2.99–3.07 (m, 2H, OC$H_2$), 3.31–3.51 (m, 2H, OC$H_2$), 4.10–4.40 (m, 8H, OC$H_2$), 4.94 (s, 5H, C$_5H_5$), 6.91–7.77 (m, 15H, PPh$_3$). $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ 46.7 (s, PPh$_3$), 118.2 (m, L$_{OEt}$). IR (cm$^{-1}$): 1296 [$\nu$(CS)]. MS (FAB): $m/z$ 978 (M$^+$). $E°$(CH$_2$Cl$_2$) = +0.520 V [Ru(III/II)].

### 3.9. [L$_{OEt}$Ru(CS)(PPh$_3$)(H$_2$O)][BF$_4$] (**8**)

To a solution of **7** (0.08 g, 0.082 mmol) in acetone–H$_2$O (40 ml, 10:1) was added AgBF$_4$ (0.025 g, 0.09 mmol). The reaction mixture was heated at reflux for 45 min and filtered. Recrystallization from CH$_2$Cl$_2$–hexane afforded yellow crystals Yield: 0.05 g (60%). Anal. Calc. for C$_{36}$H$_{52}$BCoF$_4$O$_{10}$P$_4$RuS: C, 41.26; H, 4.97. Found: C, 41.20; H, 4.72%. $^1$H-NMR (CDCl$_3$): $\delta$ 0.81 (t, 3H, C$H_3$), 0.96 (t, 3H, C$H_3$), 1.21–1.23 (overlapping, 6H, C$H_3$), 1.28 (t, 3H, C$H_3$), 1.36 (t, 3H, C$H_3$), 3.01–3.52 (m, 6H, OC$H_2$), 4.08–4.25 (m, 6H, OC$H_2$), 4.94 (s, 5H, C$_5H_5$), 6.95–7.76 (m, 15H, PPh$_3$); the resonance signal for the aqua ligand was not observed. $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ 46.0 (s, PPh$_3$), 118.2 (m, L$_{OEt}$). $^{19}$F-NMR (CDCl$_3$): $\delta$ −155.0 (BF$_4$).

### 3.10. Reaction of **8** with 4-tert-butylpyridine

To a solution of **8** (50 mg) in CH$_2$Cl$_2$ (10 ml) was added excess 4-*tert*-butylpyridine ($^t$Bupy) (0.1 ml). The reaction mixture was stirred at room temperature for 1 h and evaporated to dryness. The residue was washed with Et$_2$O to give a yellow solid, which was characterized as [L$_{OEt}$Ru(CS)(PPh$_3$)($^t$Bupy)][BF$_4$] (**9**) by NMR spectroscopy. $^1$H-NMR (CDCl$_3$): $\delta$ 0.84 (t, 3H, C$H_3$), 0.96 (t, 3H, C$H_3$), 1.21–1.33 (overlapping t, 12H, C$H_3$), 1.37 (s, 9H, $^t$Bu), 3.03–3.49 (m, 6H, OC$H_2$), 4.10–4.24 (m, 6H, OC$H_2$), 4.98 (s, 5H, C$_5H_5$), 6.91–7.64 (m, 20H, PPh$_3$ and pyridyl protons). $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ 46.0 (s, PPh$_3$), 118.2 (m, L$_{OEt}$).

Table 2
Selected bond lengths (Å) and angles (°) for [L$_{OEt}$Ru(CO)(PPh$_3$)Cl] (**3**)

| *Bond lengths* | | | |
|---|---|---|---|
| Ru(1)–C(6) | 1.993(7) | Ru(1)–O(3) | 2.118(3) |
| Ru(1)–O(2) | 2.142(3) | Ru(1)–O(1) | 2.151(3) |
| Ru(1)–P(4) | 2.2811(13) | Ru(1)–Cl(1) | 2.376(2) |
| O(10)–C(6) | 0.930(7) | | |

| *Bond angles* | | | |
|---|---|---|---|
| C(6)–Ru(1)–O(3) | 93.2(2) | C(6)–Ru(1)–O(2) | 175.8(2) |
| O(3)–Ru(1)O(2) | 85.58(13) | C(6)–Ru(1)–O(1) | 90.6(2) |
| O(3)–Ru(1)–O(1) | 86.05(12) | O(2)–Ru(1)–O(1) | 86.50(13) |
| C(6)–Ru(1)–P(4) | 88.0(2) | O(3)–Ru(1)–P(4) | 93.84(9) |
| O(2)–Ru(1)–P(4) | 94.92(10) | O(1)–Ru(1)–P(4) | 178.55(10) |
| C(6)–Ru(1)–Cl(1) | 94.1(2) | O(3)–Ru(1)–Cl(1) | 170.04(10) |
| O(2)–Ru(1)–Cl(1) | 88.74(10) | O(1)–Ru(1)–Cl(1) | 87.15(10) |
| P(4)–Ru(1)–Cl(1) | 93.13(5) | O(10)–C(6)–Ru(1) | 178.7(6) |

Table 3
Selected bond lengths (Å) and angles (°) for $[L_{OEt}Ru(\eta^2\text{-}S_2CPPh_3)(PPh_3)][BF_4][PF_6]$ (**6**)

*Bond lengths*

| | | | |
|---|---|---|---|
| Ru–O(3) | 2.070(2) | Ru–O(2) | 2.082(3) |
| Ru–O(1) | 2.083(2) | Ru–S(1) | 2.2843(9) |
| Ru–S(2) | 2.2976(9) | Ru–P(4) | 2.3978(10) |
| S(1)–C(6) | 1.691(3) | S(2)–C(6) | 1.683(3) |
| P(5)–C(6) | 1.813(3) | | |

*Bond angles*

| | | | |
|---|---|---|---|
| O(3)–Ru–O(2) | 87.04(10) | O(3)–Ru–O(1) | 87.65(10) |
| O(2)–Ru–O(1) | 88.39(10) | O(3)–Ru–S(1) | 97.94(7) |
| O(2)–Ru–S(1) | 87.07(8) | O(1)–Ru–S(1) | 172.60(7) |
| O(3)–Ru–S(2) | 171.17(7) | O(2)–Ru–S(2) | 88.92(8) |
| O(1)–Ru–S(2) | 100.09(7) | S(1)–Ru–S(2) | 74.00(3) |
| O(3)–Ru–P(4) | 93.09(7) | O(2)–Ru–P(4) | 178.42(7) |
| O(1)–Ru–P(4) | 93.19(7) | S(1)–Ru–P(4) | 91.35(3) |
| S(2)–Ru–P(4) | 90.74(4) | | |

Table 4
Selected bond lengths (Å) and angles (°) for $[L_{OEt}Ru(CS)(PPh_3)Cl]$ (**7**)

*Bond lengths*

| | | | |
|---|---|---|---|
| Ru(1)–Cl(1) | 2.3681(10) | Ru(1)–P(5) | 2.3043(9) |
| Ru(1)–O(1) | 2.141(2) | Ru(1)–O(2) | 2.174(2) |
| Ru(1)–O(3) | 2.106(2) | Ru(1)–C(6) | 1.823(4) |
| C(6)–S(1) | 1.504(4) | | |

*Bond angles*

| | | | |
|---|---|---|---|
| Cl(1)–Ru(1)–P(4) | 93.09(3) | Cl(1)–Ru(1)–O(1) | 86.84(7) |
| P(4)–Ru(1)–O(1) | 179.77(7) | Cl(1)–Ru(1)–O(2) | 88.10(7) |
| P(4)–Ru(1)–O(2) | 95.00(6) | O(1)–Ru(1)–O(2) | 85.22(8) |
| Cl(1)–Ru(1)–O(3) | 168.97(7) | P(4)–Ru(1)–O(3) | 93.01(6) |
| O(1)–Ru(1)–O(3) | 87.09(8) | O(2)–Ru(1)–O(3) | 82.22(9) |
| Cl(1)–Ru(1)–C(6) | 95.61(11) | P(4)–Ru(1)–C(6) | 86.86(10) |
| O(1)–Ru(1)–C(6) | 92.93(11) | O(2)–Ru(1)–C(6) | 175.76(12) |
| O(3)–Ru(1)–C(6) | 93.89(13) | Ru(1)–C(6)–S(1) | 178.0(2) |

## 4. Supplementary material

Crystallographic data for complexes **3**, **6** and **7** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 144169, 144170 and 144171, respectively. Copies of this information can 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).

## References

[1] W. Kläui, Angew. Chem. Int. Ed. Engl. 29 (1990) 627.
[2] See for example: U. Kölle, Coord. Chem. Rev. 134/135 (1994) 623.
[3] (a) W. Kläui, H. Otto, W. Eberspach, E. Bulcholz, Chem. Ber. 115 (1982) 1922. (b) J.M. Power, K. Evertz, L. Herling, R. Marsh, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, Inorg. Chem. 29 (1990) 5058. (c) U. Kölle, G. Flunkert, R. Gorissen, M.U. Schmidt, U. Englert, Angew. Chem. Int. Ed. Engl. 31 (1992) 440.
[4] (a) W.-H. Leung, E.Y.Y. Chan, W.-T. Wong, I.D. Williams, Organometallics 16 (1997) 3234. (b) W.-H. Leung, E.Y.Y. Chan, W.-T. Wong, Organometallics 17 (1998) 1245. (c) W.-H. Leung, E.Y.Y. Chan, W.-T. Wong, Inorg. Chem. 38 (1999) 136.
[5] H.F. Hill, Comprehensive Organometallic Chemistry II, in: E. Abel, F.G.A. Stone, G. Wilkinson (Eds.), vol. 7, Pergamon Press, Oxford, 1995, chapter 6.
[6] A.L. Hector, A.F. Hill, Inorg. Chem. 34 (1995) 3797.
[7] A.E. Kruse, R.J. Angelici, J. Organomet. Chem. 24 (1970) 231.
[8] M.I. Bruce, D.N. Sharrocks, F.G.A. Stone, J. Organomet. Chem. 31 (1971) 269.
[9] P.J. Brothers, W.R. Roper, J. Organomet. Chem. 258 (1983) 73.
[10] A. Glindo, D. Miguel, J. Perez, Coord. Chem. Rev. 193–195 (1999) 643.
[11] B. Alvarez, D. Miguel, J.A. Pérez-Martínez, V. Riera, J. Organomet. Chem. 474 (1994) 143.
[12] H. Werner, M.A. Tena, N. Mahr, K. Peters, H.-G. von Schnering, Chem. Ber. 128 (1995) 41.
[13] L.H. Pignolet, Inorg. Chem. 13 (1974) 2051.
[14] (a) T.N. Margulis, D.H. Templeton, J. Chem. Phys. 36 (1962) 2311. (b) T.N. Margulis, D.H. Templeton, J. Am. Chem. Soc. 83 (1961) 995.
[15] E. Lindner, M. Haustein, R. Fawzi, M. Steimann, P. Wegner, Organometallics 13 (1994) 5021.
[16] W. Kläui, Z. Naturforsch. Sect. B: Anorg. Chem. Org. Chem. 34B (1979) 1043.
[17] M.J. Cleare, W.P. Griffith, J. Chem. Soc. Sect. A (1969) 372.
[18] T.A. Stephenson, J. Chem. Soc. Dalton Trans. (1974) 1134.
[19] G.M. Sheldrick, SHELXL-93, Siemens Analytical Instruments, Madison, WI, 1993.

*3.11. X-ray crystallography*

A summary of crystallographic data and experimental details for complexes **3**, **6** and **7** are given in Table 1. All data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å). Absorption corrections are semi-empirical based on psi-scan data. All the structures were solved by direct methods and expanded by Fourier-difference techniques. Full-matrix least-squares refinement was based upon $F^2$. Non-hydrogen atoms were refined anisotropically. All calculations were performed using the SHELXL-93 [19] crystallographic software package.