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Monomeric and dimeric ruthenium thiooxalate complexes: Structures of $CpRu(PPh_3)_2SCOCO_2Me$ and $CpRu(dppe)SCOCO_2Et$

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Abstract

The hydrosulfido complexes CpRu(L)(L′)SH react with one equivalent of *O*-alkyl oxalyl chlorides (ROCOCOCl) to form the corresponding *O*-alkylthiooxalate complexes $CpRu(L)(L')SCOCO_2R$ ($L = L' = PPh_3$ (**1**), $\frac{1}{2}$dppe (**2**); $L = PPh_3$, $L' = CO$ (**3**); R = Me (**a**), Et (**b**)). The reactions of the hydrosulfido complexes with half equivalent of oxalyl chloride produce the bimetallic complexes $[CpRu(L)(L')SCO]_2$ ($L = L' = PPh_3$ (**4**), $\frac{1}{2}$dppe (**5**); $L = PPh_3$, $L' = CO$ (**6**)). The crystal structures of $CpRu(PPh_3)_2SCOCO_2Me$ (**1a**) and $CpRu(dppe)SCOCO_2Et$ (**2b**) are reported.

Keywords: Ruthenium; *O*-alkylthiooxalate; Sulfur; Triphenylphosphine; Diphenylphosphinoethane; Carbonyl; Complexes; Solid-state structure

1. Introduction

The coordination chemistry and reactivity of hydrosulfido metal complexes, [M]–SH, are of current interest because of their structural diversity, relevant to metalloenzymes and industrial processes such as hydrodesulfurization and Claus chemistry [1–4]. The reaction of these hydrosulfido complexes with sulfur dioxide (to give [M]-SS(O)OH) has been proposed as a key step in the Claus process [5,6] and also in the hydrogenation of sulfur dioxide [7,8].

The bis(triphenylphosphine) hydrosulfido ruthenium complex $CpRu(PPh_3)_2SH$ is prepared by a metathesis reaction of the corresponding ruthenium chloride with NaSH [9,10]. Treatment of this hydrosulfido complex with CO gas at room temperature produces the mixed carbonyl-phosphine complex $CpRu(PPh_3)(CO)SH$ in good isolated yield [9]. The chelate complexes CpRu(dppe)SH and CpRu(dppm)SH have been also reported of which the first one was prepared by a one-pot reaction of $CpRu(PPh_3)_2Cl$, dppe and NaSH, while the second one is accessible from CpRu(dppm)Cl and NaSH [11].

The ruthenium hydrosulfido complexes CpRu(L)(L′)SH are quite reactive toward a variety of electrophiles [10–12]. The reaction of $CpRu(PPh_3)_2SH$ with carbon disulfide is reported to produce the bimetallic complex $CpRu(PPh_3)$-(κ^2S,S-S_2C)$SRu(PPh_3)_2Cp$ *via* insertion of CS_2 into the Ru–S bond to give $CpRu(PPh_3)(\kappa^2S,S$-$S_2CSH)$ followed by its reaction with another equivalent of $CpRu(PPh_3)_2SH$ [10]. On the other hand, complexes CpRu(L)(L′)SH ($L = L' = PPh_3$, $\frac{1}{2}$dppm, $\frac{1}{2}$dppe) give with acid chlorides at low temperature the corresponding thiocarboxylate complexes $CpRu(L)(L')SCOCH_2$-4-C_6H_4X (X = H, Me, OMe, Cl) [12]. The mixed carbonyl-phosphine analogs $CpRu(PPh_3)(CO)SCOCH_2$-4-C_6H_4X have been prepared by the reaction of $CpRu(PPh_3)_2SCOCH_2$-4-C_6H_4X with CO [12]. The reaction of the chelate hydrosulfido complexes CpRu(dppa)SH (dppa = dppm, dppe) with various sulfonyl chlorides afforded the expected thiosulfonato species $CpRu(L)(L')SSO_2R$ [13]. Recently, the reaction of these hydrosulfido complexes with chloroformates

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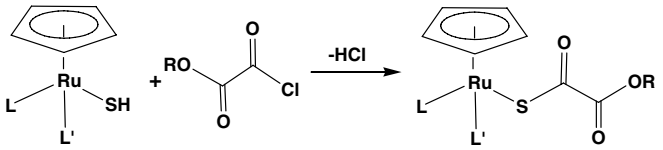
(ROCOCl) were found to produce the appropriate thiocarbonate complexes $CpRu(L)(L')SCO_2R$ ($L = L' = PPh_3$, $\frac{1}{2}$dppe; $L = PPh_3$, $L' = CO$; R = alkyl, aryl) [14].

As an extension to our work in this area, we here describe the synthesis of some monomeric half sandwich ruthenium complexes containing *O*-alkylthiooxalate ligands and dimeric ruthenium complexes containing thiooxalate ligands.

2. Results and discussion

2.1. Synthesis

The ruthenium complexes $CpRu(L)(L')SCOCO_2R$ (**1**–**3**) are readily prepared by condensation of the hydrosulfido complexes $CpRu(L)(L')SH$ with *O*-alkyl oxalyl chlorides as shown in the following equation:



L = L´ = PPh_3 (**1**), ½dppe (**2**); L= PPh_3, L´ = CO (**3**)

R = Me (**a**), Et (**b**)

(1)

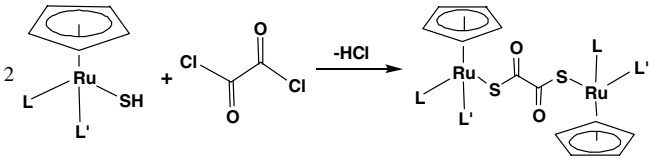
Complexes **1**–**3** are yellow to orange colored solids and were identified by IR, ^1H, ^{31}P NMR spectroscopy, elemental analysis and X-ray structure determination for **1a** and **2b**. These new complexes are soluble in common organic solvents and insoluble in hydrocarbons. They are quite stable as solids and in solution. There is no need for a base to be added for these reactions to remove the produced HCl indicating of the robustness of the products toward hydrolysis with HCl.

The IR spectra of the newly prepared complexes **1**–**3** show two medium bands in the ranges of 1720–1730 cm^{-1} (OC═O) and 1580–1611 cm^{-1} (SC═O) for the ketonic carbonyl groups of the *O*-alkylthiooxalato ligands. Although the OC═O frequencies for complexes **1**–**3** are comparable to each other, the $\nu_{SC=O}$ frequencies in these complexes are sensitive to the ligands coordinated to the Ru center (L and L′). For **1**, the $\nu_{SC=O}$ vibration is in the range of 1580–1581 cm^{-1}, which is lower than that of **2** (1590–1591 cm^{-1}) and this is lower than that of **3** (1609–1611 cm^{-1}). These ligand-dependent frequencies are also found in the thiocarboxylate analogs [12] and may be due to a less electron density around the ruthenium in **3**, compared to that of **1** and **2**. This can nicely be reflected by the CO vibrations. Each of these ranges is lower than the corresponding range reported for the thiocarboxylate analogs ($CpRu(L)(L')SCOR$: $L = L' = PPh_3$ (1598–1610 cm^{-1}), $\frac{1}{2}$dppe (1595–1624 cm^{-1}); $L = PPh_3$, $L' = CO$ (1636 cm^{-1})) [12]. The spectra of **3** also contain a strong band at 1967 cm^{-1} for the terminal carbonyl group bonded to ruthenium. This band is similar to that found for $CpRu(PPh_3)(CO)SCOPh$ (1961 cm^{-1}) [12].

The ^1H NMR spectra of complexes **1**–**3** typically display a singlet for the Cp protons at 4.56 and between 4.71–4.72 and 4.97–4.98 ppm. Variation associated with changing the R group has negligible effects on the Cp-peaks in the NMR spectra of these complexes. These data are in good agreement with those reported for similar systems ($CpRu(L)(L')SCOR$ [12], $CpRu(L)(L')SR$ [15,16]).

The ^{31}P NMR spectra of **1**–**3** reflect changes in the ligand type around ruthenium. For complexes **1** and **2** a singlet is observed between 46.57–46.59 ppm and 86.19–86.30 ppm, respectively, for the two identical phosphorus atoms. The strong π-acid ligand (CO) in **3** deshields the PPh_3 phosphorus atom (55.68–55.76 ppm), compared to that of **1**, similar to the Cp peak in the ^1H NMR spectra of **3** (vide supra). The ^{31}P NMR data are comparable to those reported for thiolate and thiocarboxylate ruthenium species [12,15,16].

The reaction of $CpRu(L)(L')SH$ with oxalyl chloride in a 2:1 molar ratio results in the formation of the ruthenium dimers $[CpRu(L)(L')SCO]_2$ (**4**–**6**) as shown in the following equation:



L = L´ = PPh_3 (**4**), ½ dppe (**5**); L= PPh_3, L′= CO (**6**)

(2)

Complexes **4**–**6** were characterized by IR, ^1H, ^{31}P NMR spectroscopy and elemental analysis. As expected, the IR spectra of **4**–**6** display characteristic bands in the range of 1721–1743 cm^{-1} which can be assigned to the stretching vibrations of the thiocarboxylate CO group. The vibration of each of these complexes is shifted to higher wavenumbers in comparison to the analogous typical band for **1**–**3**. Complex **6** shows another strong absorption at 1967 cm^{-1} for the terminal carbonyl group in its IR spectrum. This band is similar to those observed for **3**. The ^1H NMR spectra of **4**, **5** and **6** show a singlet for the Cp ring protons comparable to the analogous peak for **1**–**3**, respectively. The ^{31}P NMR spectra of **4**–**6** display a singlet at 46.19, 86.19 and 55.57 ppm, respectively. These peaks are similar to those of **1**, **2** and **3.**

2.2. Crystal structures of *1a* and *2b*

Perspective views, together with the atomic numbering schemes, of $CpRu(PPh_3)_2SCOCO_2Me$ (**1a**) and $CpRu(dppe)SCOCO_2Et$ (**2b**) are shown in Figs. 1 and 2, respectively. Selected bond lengths (Å) and bond angles (°) of these complexes are summarized in Table 1. The coordination around ruthenium in both complexes confirms to a typical piano stool structure in which the Cp ring is bonded to ruthenium

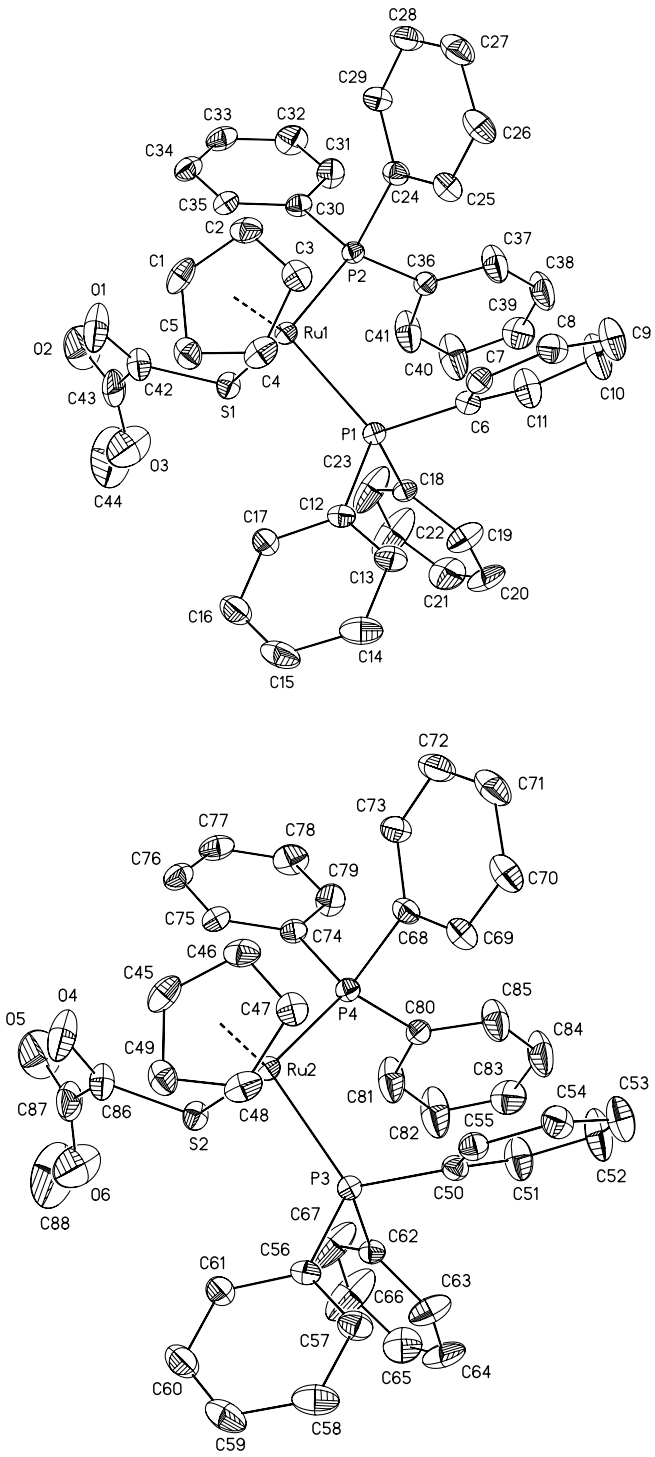


Fig. 1. ORTEP drawing of $CpRu(PPh_3)_2SCOCO_2Me$ (**1a**).

in an η^5-fashion. The geometry of the CpRu(L)(L′) moiety is similar to that observed for other related complexes [15–18]. The Ru–S bond distances of **1a** (2.3930(12), 2.3940(13) Å) and of **2b** (2.3768(6) Å) are slightly shorter than those of known Ru-thiolato complexes, e.g., $CpRu(PPh_3)_2SC{\equiv}CPh$ (2.4216(7) Å) [17] and $CpRu(PPh_3)_2SSiPr^i_3$ (2.462(3) Å) [18]. However, these Ru–S bond distances are similar to that reported for $CpRu(dppm)SCOCH_2Ph$ (2.3819(10) Å) [12]. The Ru–P bond lengths in **1a** (average 2.3374 Å) are similar to those of thiolate analogs [17,18]. However, the analogous Ru–P bond distances of **2b** (2.2772(6), 2.2527(6) Å) which are also comparable to those of $CpRu(dppm)SCOCH_2Ph$ (2.2534(9), 2.2867(9) Å) [12] are shorter than those of **1a**. This trend is normal for complexes containing two triphenylphosphine ligands compared to those having only one diphosphine ligand. The (S)C=O bond lengths of 1.224(3) Å for **2b** is clearly longer than the (O)C=O (1.206(3) Å) length in the same molecule. However, for **1a** the situation is somewhat different; for one molecule these C=O bond lengths are almost equal [(S)C=O: 1.210(7) vs. (O)C=O (1.209(9) Å)] while for the other the (O)C=O distance is longer than the (S)C=O [(S)C=O: 1.202(7) vs. (O)C=O (1.234(9) Å)]. The corresponding (S)C=O bond length of $CpRu(dppm)SCOCH_2Ph$ is 1.211(4) Å [12].

3. Experimental

All synthetic operations were carried out under nitrogen atmosphere using Schlenk line techniques. Tetrahydrofuran (THF), diethyl ether and hexane were dried and distilled over sodium/benzophenone. Complexes CpRu(L)(L′)SH were prepared according to reported procedures [9–11]. *O*-alkyl oxalyl chlorides, oxalyl chloride and ruthenium chloride trihydrate were obtained from ACROS and used without further purification. Infrared spectra were recorded on a Bruker 410 FT-IR spectrophotometer in CH_2Cl_2 solutions using NaCl windows. ^1H and ^{31}P NMR spectra were recorded using a Bruker AVANCE 400 MHz spectrometer. Chemical shifts are quoted in ppm downfield of TMS and referenced using the chemical shifts of residual solvent resonances. Elemental analyses were performed by the Institute of Organic and Macromolecular Chemistry, FSU-Jena. Melting points were recorded on a Stuart Melting point apparatus and are uncorrected.

3.1. General procedure for the preparation of $CpRu(L)(L')SCOCO_2R$ (*1* and *2*)

The respective hydrosulfido ruthenium complexes CpR(L)(L′)SH (0.50 mmol) were dissolved in 15.0 mL of THF in a Schlenk tube and were cooled to −78 °C. A THF-solution of methyl- or ethyl oxalyl chloride (0.52 mmol) was added dropwise at the same temperature. The resulting mixture was stirred for 30 min at this temperature. The volume of the solution was concentrated under vacuum at room temperature to about 2.0 mL and was introduced to a silica gel column made up in hexane. Elution with hexane removed the excess *O*-alkyl oxalyl chloride, and with (1:1 v:v) ratio of diethyl ether:hexane gave a yellow band of the products which was collected, dried and recrystallized from THF/hexane.

3.1.1. $CpRu(PPh_3)_2SCOCO_2Me$ (*1a*)

Yellow crystals (90%). m.p.: 105–106 °C. IR (CH_2Cl_2, cm^{-1}): $\nu_{OC=O}$ 1725 (m); $\nu_{SC=O}$ 1581 (m). ^1H NMR

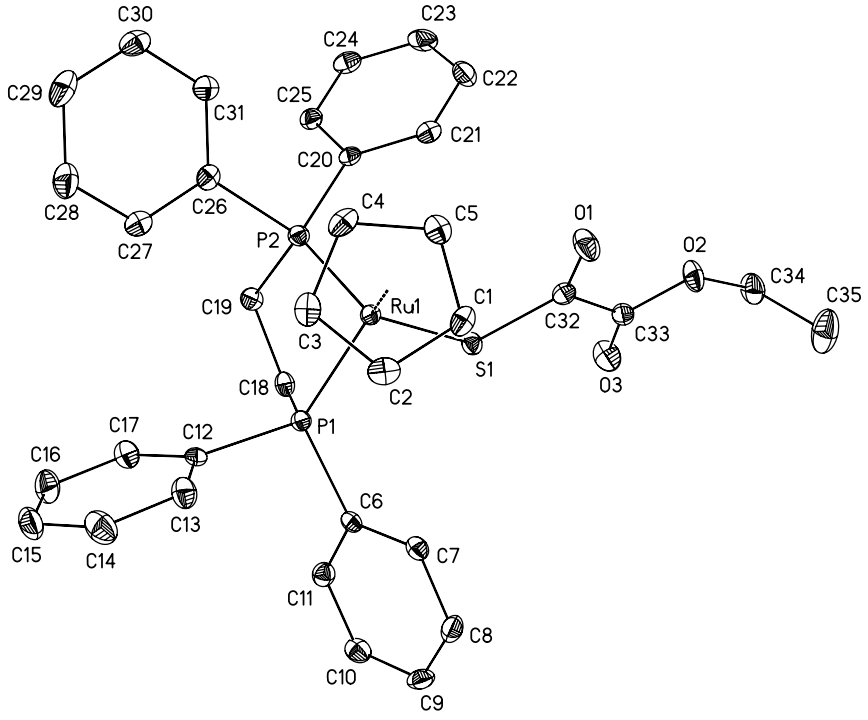


Fig. 2. ORTEP drawing of CpRu(dppe)$SCOCO_2Et$ (**2b**).

Table 1
Selected bond length (Å) and selected bond angles (°) of $CpRu(PPh_3)_2SCOCO_2Me$ (**1a**) and CpRu(dppe)$SCOCO_2Et$ (**2b**)

1a				**2b**	
Ru1–C1	2.228(5)	Ru2–C45	2.225(5)	Ru–C1	2.251(2)
Ru1–C2	2.225(5)	Ru2–C46	2.225(5)	Ru–C2	2.246(2)
Ru1–C3	2.218(5)	Ru2–C47	2.213(5)	Ru–C3	2.201(2)
Ru1–C4	2.220(4)	Ru2–C48	2.218(4)	Ru–C4	2.201(2)
Ru1–C5	2.230(5)	Ru2–C49	2.232(5)	Ru–C5	2.228(2)
Ru1–P1	2.3395(12)	Ru2–P3	2.3359(12)	Ru–P1	2.2772(6)
Ru1–P2	2.3356(12)	Ru2–P4	2.3409(12)	Ru–P2	2.2527(6)
Ru1–S1	2.3930(12)	Ru2–S2	2.3940(13)	Ru–S1	2.3768(6)
S1–C42	1.716(6)	S2–C86	1.707(6)	S1–C32	1.717(2)
C42–O1	1.202(7)	C86–O4	1.210(7)	C32–O1	1.224(3)
C43–O2	1.234(9)	C87–O5	1.209(9)	C33–O3	1.206(3)
C42–C43	1.539(10)	C86–C87	1.544(9)	C32–C33	1.544(3)
C43–O3	1.213(9)	C87–O6	1.217(9)	C33–O3	1.334(3)
C44–O3	1.526(10)	C88–O6	1.493(10)	C34–O3	1.456(3)
P1–Ru1–P2	98.80(4)	P3–Ru2–P4	98.82(4)	P1–Ru–P2	82.91(2)
P1–Ru1–S1	91.76(4)	P3–Ru2–S2	91.69(4)	P1–Ru–S1	83.03(2)
P2–Ru1–S1	91.42(5)	P4–Ru2–S2	91.42(5)	P2–Ru–S1	91.55(2)
C42–S1–Ru1	115.1(2)	C86–S2–Ru2	115.1(2)	C32–S1–Ru	111.90(8)
O1–C42–C43	116.2(6)	O4–C86–C87	114.9(6)	O1–C32–C33	119.5(2)
O1–C42–S1	130.8(5)	O4–C86–S2	130.9(5)	O1–C32–S1	128.84(18)
O2–C43–O3	123.8(9)	O5–C87–O6	123.2(9)	O2–C33–O3	124.6(2)
C43–C42–S1	112.5(5)	C87–C86–S2	113.3(5)	C33–C32–S1	111.64(16)
C43–O3–C44	111.3(8)	C87–O6–C88	112.3(9)	C33–O2–C34	118.28(18)
O2–C43–C42	119.9(8)	O5–C87–C86	119.9(8)	O2–C33–C32	110.26(19)
O1–C42–C43–O2	40.1(10)	O4–C86–C87–O5	38.1(11)	O1–C32–C33–O3	−178.6(2)

($CDCl_3$): δ 3.74 (s, 3H, CH_3); 4.56 (s, 5H, C_5H_5); 7.12 (m, 30H, PPh_3). ^{31}P NMR ($CDCl_3$): δ 46.59. Anal. Calc. for $C_{44}H_{40}O_3P_2RuS \cdot 0.5THF$: C, 65.31; H, 5.00; S, 3.79. Found: C, 64.80; H, 5.29; S, 3.71%.

3.1.2. *CpRu(PPh_3)$_2SCOCO_2Et$ (**1b**)*

Yellow crystals (87%). m.p.: 100–102 °C. IR (CH_2Cl_2, cm^{-1}): $\nu_{OC=O}$ 1720 (m); $\nu_{SC=O}$ 1580 (m). ^1H NMR ($CDCl_3$): δ 1.33 (t, 3H, CH_3); 4.19 (q, 2H, CH_2); 4.56 (s,

5H, C_5H_5); 7.14 (m, 30H, PPh_3). ^{31}P NMR ($CDCl_3$): δ 46.57. Anal. Calc. for $C_{45}H_{40}O_3P_2RuS \cdot 2THF$: C, 65.76; H, 5.83; S, 3.31. Found: C, 64.84; H, 5.27; S, 3.46%.

3.1.3. CpRu(dppe)SCOCO$_2$Me (**2a**)

Yellow crystals (85%). m.p.: 191–193 °C. IR (CH_2Cl_2, cm^{-1}): $\nu_{OC=O}$ 1724 (m); $\nu_{SC=O}$ 1591 (m). ^1H NMR ($CDCl_3$): δ 2.54 (m, 2H, CH_2PPh_2); 2.77 (m, 2H, CH_2PPh_2); 3.71 (s, 3H, CH_3); 4.71 (s, 5H, C_5H_5); 7.17 (m, 12H, PPh_2); 7.31 (m, 8H, PPh_2). ^{31}P NMR ($CDCl_3$): δ 86.30. Anal. Calc. for $C_{34}H_{32}O_3P_2RuS$: C, 59.73; H, 4.72; S, 4.69. Found: C, 58.91; H, 4.82; S, 4.22%.

3.1.4. CpRu(dppe)SCOCO$_2$Et (**2b**)

Yellow crystals (83%). m.p.: 181–182 °C. IR (CH_2Cl_2, cm^{-1}): $\nu_{OC=O}$ 1720 (m); $\nu_{SC=O}$ 1592 (m). ^1H NMR ($CDCl_3$): δ 1.42 (t, 3H, CH_3); 2.43 (m, 2H, CH_2PPh_2); 2.76 (m, 2H, CH_2PPh_2); 4.30 (q, 2H, CH_2); 4.72 (s, 5H, C_5H_5); 7.19 (m, 12H, PPh_2); 7.32 (m, 8H, PPh_2). ^{31}P NMR ($CDCl_3$): δ 86.19. Anal. Calc. for $C_{35}H_{34}O_3P_2RuS$: C, 60.25; H, 4.90; S, 4.60. Found: C, 59.96; H, 5.02; S, 4.23%.

3.1.5. CpRu(PPh$_3$)(CO)SCOCO$_2$Me (**3a**)

Yellow crystals (80%). m.p.: 221–222 °C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1967 (s); $\nu_{OC=O}$ 1730 (m); $\nu_{SC=O}$ 1609 (m). ^1H NMR ($CDCl_3$): δ 3.76 (s, 3H, CH_3); 4.98 (s, 5H, C_5H_5); 7.36 (m, 15H, PPh_3). ^{31}P NMR ($CDCl_3$): δ 55.68. Anal. Calc. for $C_{27}H_{23}O_4PRuS$: C, 56.34; H, 4.03; S, 5.57. Found: C, 56.26; H, 4.09; S, 5.26%.

3.1.6. CpRu(PPh$_3$)(CO)SCOCO$_2$Et (**3b**)

Yellow crystals (75%). m.p.: 191–192 °C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1967 (s); $\nu_{OC=O}$ 1725 (m); $\nu_{SC=O}$ 1611 (m). ^1H NMR ($CDCl_3$): δ 1.32 (t, 3H, CH_3); 4.18 (q, 2H, CH_2); 4.97 (s, 5H, C_5H_5); 7.35 (m, 15H, PPh_3). ^{31}P NMR ($CDCl_3$): δ 55.76. Anal. Calc. for $C_{28}H_{25}O_4PRuS$: C, 57.04; H, 4.23; S, 5.44. Found: C, 56.81; H, 4.35; S, 5.09%.

3.2. General procedure for the preparation of [CpRu(L)(L′)SCO]$_2$ (**4**–**6**)

These complexes were prepared in a similar way to that used for the preparation of **1**–**3** (Section 3.1). Oxalyl chloride (0.25 mmol) was used. The products were eluted with pure diethyl ether.

3.2.1. [CpRu(PPh$_3$)$_2$SCO]$_2$ (**4**)

Yellow crystals (73%). m.p.: 95–96 °C. IR (CH_2Cl_2, cm^{-1}): $\nu_{SC=O}$ 1721 (m). ^1H NMR ($CDCl_3$): δ 4.68 (s, 5H, C_5H_5); 7.41 (m, 30H, PPh_3). ^{31}P NMR ($CDCl_3$): δ 46.57. Anal. Calc. for $C_{42}H_{35}OPRuS$: C, 67.19; H, 4.70; S, 4.27. Found: C, 66.93; H, 5.02; S, 3.89%.

3.2.2. [CpRu(dppe)SCO]$_2$ (**5**)

Orange crystals (64%). m.p.: 166–167 °C. IR (CH_2Cl_2, cm^{-1}): $\nu_{SC=O}$ 1743 (m). ^1H NMR ($CDCl_3$): δ 2.50 (m, 2H, CH_2PPh_2); 2.73 (m, 2H, CH_2PPh_2); 4.72 (s, 5H, C_5H_5); 7.29 (m, 12H, PPh_2); 7.44 (m, 8H, PPh_2). ^{31}P NMR ($CDCl_3$): δ 86.16. Anal. Calc. for $C_{32}H_{29}OPRuS$: C, 61.53; H, 4.68; S, 5.13. Found: C, 60.91; H, 4.28; S, 4.90%.

3.2.3. [CpRu(PPh$_3$)(CO)SCO]$_2$ (**6**)

Orange crystals (60%). m.p.: 65–66 °C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1967 (s); $\nu_{SC=O}$ 1726 (m). ^1H NMR ($CDCl_3$): δ 4.98 (s, 5H, C_5H_5); 7.38 (m, 15H, PPh_3). ^{31}P NMR ($CDCl_3$): δ 55.77. Anal. Calc. for $C_{25}H_{20}O_2PRuS$: C, 58.13; H, 3.90; S, 6.21. Found: C, 57.50; H, 3.78; S, 6.00%.

3.3. Crystallographic analysis of CpRu(PPh$_3$)$_2$SCOCO$_2$Me (**1a**) and CpRu(dppe)SCOCO$_2$Et (**2b**)

The crystal data are shown in Table 2. Data for **1a** and **2b** were collected on an Oxford Gemini S diffractometer at 100 K using Mo Kα radiation ($\lambda = 0.71073$ Å). Both structures were solved by direct methods using SHELXS-97 [19] and refined by full-matrix least-square procedures on F_o^2 using SHELX-97 [20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions have been refined using the atom corresponded riding model. The asymmetric unit of **1a** comprises two independent molecules together with two THF molecules as packing solvents, each having an occupation factor of 0.5.

Table 2
Selected crystal data and refinement parameters for CpRu(PPh$_3$)$_2$SCOCO$_2$Me (**1a**) and CpRu(dppe)SCOCO$_2$Et (**2b**)

	1a	**2b**
Empirical formula	$C_{46}H_{42}O_{3.5}P_2RuS$	$C_{35}H_{34}O_3P_2RuS$
Formula weight (g mol^{-1})	845.87	697.69
Crystal size (mm)	$0.3 \times 0.2 \times 0.2$	$0.2 \times 0.1 \times 0.05$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
Volume (Å^3)	4282(1)	3135.6(5)
Z	4	4
Unit cell dimensions		
a (Å)	12.932(1)	11.6283(11)
b (Å)	14.753(3)	23.0039(17)
c (Å)	26.124(4)	12.8614(12)
α (°)	75.367(1)	90
β (°)	75.703(7)	114.299(9)
δ (°)	64.026(6)	90
Index range	$-15 \leqslant k \leqslant 15$	$-13 \leqslant h \leqslant 13$
	$-18 \leqslant k \leqslant 18$	$-27 \leqslant k \leqslant 27$
	$-32 \leqslant l \leqslant 32$	$-15 \leqslant l \leqslant 15$
Radiation type	Mo Kα	Mo Kα
Density (Mg m^{-3})	1.312	1.478
μ (mm^{-1})	0.529	0.703
θ (°)	2.90–26.06	3.17–25.20
λ (Å)	0.71073	0.71073
$R[F^2 > 2\sigma(F^2)]$	0.0485	0.0242
$\omega R(F^2)$[a]	0.1547	0.0443

[a] $\omega = 1/[\sigma^2(F_o^2) + (0.1007P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

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Appendix A. Supplementary materials

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (Deposition Nos. CCDC 600974 and 600975) for compounds **1a** and **2b**, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.018.

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