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Sulfur(IV) compounds as ligands[☆] Part XXV. Halfsandwich ruthenium thiosulfonato complexes. Crystal and molecular structure of [CpRu(dppe){$SSO_2(4\text{-}C_6H_4Cl)$}]

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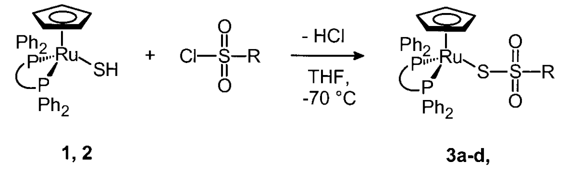
Abstract

Reaction of the hydrogen sulfido complexes [CpRu(P–P)(SH)] (P–P = dppm (**1**), dppe (**2**)) with sulfonyl chlorides RSO_2Cl at − 70°C in THF gave the ruthenium thiosulfonato complexes [CpRu(P–P)(SSO_2R)] (P–P = dppm (**3**), dppe (**4**), R = Me (**a**), Ph (**b**), 4-C_6H_4Cl (**c**), 4-$C_6H_4NO_2$ (**d**)). The structure of **4c** was determined by X-ray crystallography. Important molecular geometry data are: Ru–S(1) 239.3(2), S(1)–S(2) 203.2(2), S(2)–O(1) 145.0(5), S(2)–O(2) 144.1(5) pm; Ru–S(1)–S(2) 104.23(8)°. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Phosphines; Ruthenium; Structure; Sulfur; Thiosulfonate

1. Introduction

Transition metal complexes containing sulfur–sulfur bonds provide a fascinating field of study. Apart from the surprising variety of possible structures [2–9] they serve as models for metal-mediated sulfur transfer reactions in organic syntheses [10–12] as well as the removal of sulfur from petroleum products [13,14]. Partially oxygenated derivatives contain the oxygen preferentially as branched sulfoxide (–S(O)–) units [15–18]; thus far, only one example of a compound containing a linear M–O–S–S– unit (M = Ti) has been structurally characterized [18]. Due to the intrinsic lability of sulfur–sulfur bonds such complexes are invariably prone to rearrangement and sulfur redistribution reactions. That is why specific syntheses as well as unambiguous characterization of products often remains a challenge. A number of thiosulfinato complexes L_nM–S–S(O)–R (M = Ru, Pt) have recently been prepared and their structures determined by X-ray crystallography [19–24]. One of those compounds was found upon prolonged heating to undergo a disproportionation reaction to the corresponding disulfano and thiosulfonato complexes, respectively. The latter had been identified by X-ray crystallography [19]. This seems to indicate that thiosulfonato complexes are a class of fairly stable compounds which should be accessible by more direct routes. In the following, we describe the synthesis of some ruthenium halfsandwich complexes containing methyl and aryl thiosulfonato ligands and the determination of the structure of one of them.



1, 2

3a-d, 4a-d

$Ph_2P\frown PPh_2$	Me	Ph	4-C_6H_4Cl	4-$C_6H_4NO_2$
$Ph_2PCH_2PPh_2$	**3a**	**3b**	**3c**	**3d**
$Ph_2PC_2H_4PPh_2$	**4a**	**4b**	**4c**	**4d**

Scheme 1. Synthesis of thiosulfonato complexes **3a**–**d** and **4a**–**d** from hydrogen sulfido complexes and sulfonyl chlorides.

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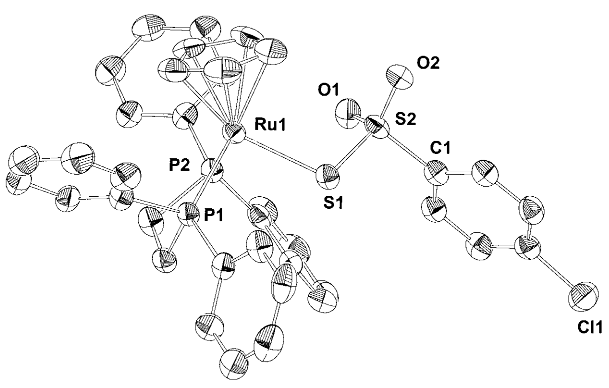

Fig. 1. Molecular structure of [CpRu(dppe){$SSO_2(4\text{-}C_6H_4Cl)$}] (**4c**). Hydrogen atoms omitted for clarity.

Table 1
Selected bond distances (pm) and angles (°) for [CpRu(dppe){$SSO_2(4\text{-}C_6H_4Cl)$}] (**4c**)

Atoms	Bond distance	Atoms	Bond angle
Ru–S(1)	239.3(2)	P(1)–Ru–P(2)	83.45(6)
Ru–P(1)	227.49(15)	P(1)–Ru–S(1)	93.50(6)
Ru–P(2)	228.85(18)	P(2)–Ru–S(1)	94.81(6)
Ru–C(50)	224.5(10)	Ru–S(1)–S(2)	104.23(8)
Ru–C(51)	224.4(9)	S(1)–S(2)–O(1)	112.2(2)
Ru–C(52)	219.0(9)	S(1)–S(2)–O(2)	110.7(2)
Ru–C(53)	220.1(8)	S(1)–S(2)–C(1)	103.6(2)
Ru–C(54)	221.8(7)	O(1)–S(2)–O(2)	115.4(3)
S(1)–S(2)	203.2(2)	O(1)–S(2)–C(1)	107.1(3)
S(2)–O(1)	145.0(5)	O(2)–S(2)–C(1)	106.9(3)
S(2)–O(2)	144.1(5)		
S(2)–C(1)	176.7(7)		

2. Results

2.1. Synthesis

The reaction of the hydrogen sulfido complexes **1**, **2** with various sulfonyl chlorides at −70°C in THF afforded the expected thiosulfonato complexes **3a**–**d** and **4a**–**d** in good yields (Scheme 1).

The new compounds are air-sensitive yellow or orange crystalline compounds which are soluble in most of the common organic solvents except aliphatic hydrocarbons. Their proton NMR spectra show the expected signals of the Cp, phosphine, and R groups, respectively. The ^{31}P-NMR spectra consist of singlets in the typical region [25] around 11 ppm (dppm complexes **3a**–**d**) and 78 ppm (dppe complexes **4a**–**d**). The sulfonyl group reveals its presence through a strong absorption in the infrared spectra at 1255 cm^{-1} due to the asymmetric $\nu(SO_2)$. The weaker symmetric $\nu(SO_2)$, expected around 1100 cm^{-1}, was masked by other ligand vibrations.

2.2. Structure determination of [CpRu(dppe){$SSO_2(4\text{-}C_6H_4Cl)$}] (4c)

An orange crystal of **4c** was subjected to an X-ray structure determination, the result of which is shown in Fig. 1. Important interatomic distances and angles are given in Table 1.

The Ru–S(1) distance is very similar to those in comparable ruthenium–thiosulfinate [19–21] and thiocarboxylate complexes [26]. The S(1)–S(2) distance, on the other hand, is about 4 pm smaller than in those compounds and comparable to the corresponding distance in the other known thiosulfonate complex [19]. The angle Ru–S(1)–S(2) falls in the expected range, and as yet no clear trend on going from thiosulfinate to thiosulfonate complexes emerges. The rotational arrangement of the phenyl groups of the phosphine ligand follows the familiar 'edge-face' pattern which dominates steric interactions in complexes of this type [27].

3. Discussion

The preparation of the new thiosulfonato complexes (Scheme 1) is closely analogous to the synthesis of similar ruthenium thiocarboxylate complexes from Ru–SH compounds and acyl halides [26]. The reaction proceeds readily at low temperature and does not even require added base to remove the liberated hydrogen chloride. This attests to the high nucleophilicity of the starting Ru–SH complexes as well as the chemical inertness of the products. The structure determination of **4c** unambiguously proves the identity of the new compounds. Specifically, no oxygen redistribution or migration along the S–S bond, which in principle is a facile process in organic [28] as well as organometallic polysulfides [17–19], has taken place. The shortening of the S–S bond in comparison with thiosulfinato complexes is certainly due to the contraction of the valence orbitals of S(2) brought about by the attachment of a second electronegative oxygen substituent. The S–O bond lengths do not reveal any clear trend outside the usual 3σ criterion. Nevertheless, the low $\nu(SO_2)$ at 1255 cm^{-1} (cf. $MeSSO_2Me$, $\nu(SO_2)$ 1315 (as), 1130 (sy) cm^{-1} [29]) hints at a considerable transmission of electron density from the electropositive transition metal via S(1) all the way into the sulfone group.

4. Experimental

All manipulations were carried out in Schlenk-type glassware under an atmosphere of purified nitrogen. Solvents were dried with sodium–potassium alloy and distilled under nitrogen prior to use. NMR solvents were degassed and stored over molecular sieves and under nitrogen. NMR spectra were recorded using a JEOL JNM-LA 300 instrument (^{1}H: 300 MHz, TMS, ^{31}P: 121.5 MHz, H_3PO_4). ^{1}H-NMR signals of the aryl groups and the phosphine ligands are uncharacteristic and are therefore omitted from the lists of spectral data. IR spectra were recorded on a Bruker IFS 25 instrument. Melting or decomposition points were determined by differential scanning calorimetry (DSC) using a Du Pont 9000 thermal analyzer. The hydrogen sulfido complexes **1**, **2** were obtained using a suitably adapted published method [30,31]. All other reagents were used as obtained commercially.

4.1. Synthesis of the thiosulfonato complexes: general procedure

To a solution of the hydrogen sulfido complex **1** (95 mg, 0.16 mmol) or **2** (100 mg, 0.16 mmol) in THF (10 ml) a solution of the respective sulfonyl chloride (0.16 mmol) in THF (10 ml) was slowly added at −70°C. The mixture was allowed to warm to 20°C and concentrated under vacuum to 2 ml. The residue was chromatographed over silica eluting with THF–hexane 1:1. The broad yellow band was collected and evaporated to dryness and the crude product recrystallized from THF–hexane.

*4.2. [CpRu(dppm)(SSO$_2$CH$_3$)] (**3a**)*

Yield 70 mg (65%), yellow crystalline powder, m.p. 108°C. IR (cm^{-1}, Nujol): 1259 (ν(SO)$_{as}$). ^{1}H-NMR (acetone-d_6): δ 2.10 (s, 3H, CH_3), 5.03 (s, 5H, C_5H_5). ^{31}P-NMR (acetone-d_6): δ 11.1 (s). Anal. Calc. for $C_{31}H_{30}O_2P_2RuS_2$ (661.7): C, 56.27; H, 4.57; S, 9.69. Found: C, 55.65; H, 4.59; S, 9.17%.

*4.3. [CpRu(dppm)(SSO$_2$C$_6$H$_5$)] (**3b**)*

Yield 80 mg (68%), yellow crystalline powder, m.p. 125°C. IR (cm^{-1}, Nujol): 1252 (ν(SO)$_{as}$). ^{1}H-NMR (acetone-d_6): δ 5.00 (s, 5H, C_5H_5). ^{31}P-NMR (acetone-d_6): δ 10.9 (s). Anal. Calc. for $C_{36}H_{32}O_2P_2RuS_2$ (723.8): C, 59.74; H, 4.46; S, 8.86. Found: C, 59.43; H, 4.16; S, 8.73%.

*4.4. [CpRu(dppm){SSO$_2$(4-C$_6$H$_4$Cl)}] (**3c**)*

Yield 90 mg (75%), red crystals, m.p. 118°C. IR (cm^{-1}, Nujol): 1253 (ν(SO)$_{as}$). ^{1}H-NMR (acetone-d_6): δ 5.01 (s, 5H, C_5H_5). ^{31}P-NMR (acetone-d_6): δ 10.7 (s). Anal. Calc. for $C_{36}H_{31}ClO_2P_2RuS_2$ (758.2): C, 57.03; H, 4.12; S, 8.46. Found: C, 57.69; H, 4.50; S, 7.44%.

*4.5. [CpRu(dppm){SSO$_2$(4-C$_6$H$_4$NO$_2$)}] (**3d**)*

Yield 95 mg (78%), brown crystals, m.p. 118°C. IR (cm^{-1}, Nujol): 1253 (ν(SO)$_{as}$). ^{1}H-NMR (acetone-d_6): δ 5.05 (s, 5H, C_5H_5). ^{31}P-NMR (acetone-d_6): δ 10.3 (s). Anal. Calc. for $C_{36}H_{31}NO_4P_2RuS_2$ (768.8): C, 56.24; H, 4.06; S, 8.34. Found: C, 55.77; H, 4.69; S, 7.88%.

*4.6. [CpRu(dppe)(SSO$_2$CH$_3$)] (**4a**)*

Crystallization from dichloromethane–hexane gave a dichloromethane solvate. Yield 88 mg (72%), yellow crystalline powder, m.p. 196°C. IR (cm^{-1}, Nujol): 1266 (ν(SO)$_{as}$). ^{1}H-NMR (acetone-d_6): δ 1.41 (s, 3H, CH_3), 4.84 (s, 5H, C_5H_5). ^{31}P-NMR (acetone-d_6): δ 77.3 (s). Anal. Calc. for $C_{32}H_{32}O_2P_2RuS_2{\cdot}CH_2Cl_2$ (760.7): C, 52.11; H, 4.51; S, 8.45. Found: C, 53.07; H, 4.33; S, 8.44%.

*4.7. [CpRu(dppe)(SSO$_2$C$_6$H$_5$)] (**4b**)*

Yield 92 mg (78%), yellow crystalline powder, m.p. 220°C. IR (cm^{-1}, Nujol): 1253 (ν(SO)$_{as}$). ^{1}H-NMR (acetone-d_6): δ 4.64 (s, 5H, C_5H_5). ^{31}P-NMR (acetone-d_6): δ 78.4 (s). Anal. Calc. for $C_{37}H_{34}O_2P_2RuS_2$ (737.8): C, 60.23; H, 4.65; S, 8.69. Found: C, 59.91; H, 4.56; S, 8.56%.

*4.8. [CpRu(dppe){SSO$_2$(4-C$_6$H$_4$Cl)}] (**4c**)*

Yield 105 mg (84%), orange crystals, m.p. 204°C. IR (cm^{-1}, Nujol): 1253 (ν(SO)$_{as}$). ^{1}H-NMR (acetone-d_6): δ 4.68 (s, 5H, C_5H_5). ^{31}P-NMR (acetone-d_6): δ 78.11 (s). Anal. Calc. for $C_{37}H_{33}ClO_2P_2RuS_2$ (772.2): C, 57.55; H, 4.31; S, 8.30. Found: C, 57.44; H, 4.14; S, 7.99%.

*4.9. [CpRu(dppe){SSO$_2$(4-C$_6$H$_4$NO$_2$)}] (**4d**)*

Yield 105 mg (85%), brown crystals, m.p. 230°C. IR (cm^{-1}, Nujol): 1255 (ν(SO)$_{as}$). ^{1}H-NMR (acetone-d_6): δ 4.67 (s, 5H, C_5H_5). ^{31}P-NMR (acetone-d_6): δ 77.7 (s). Anal. Calc. for $C_{37}H_{33}NO_4P_2RuS_2$ (782.8): C, 56.77; H, 4.25, N 1.79; S, 8.19. Found: C, 56.10; H, 4.53, N 1.68; S, 7.75%.

*4.10. Crystal structure determination of [CpRu(dppe){SSO$_2$(4-C$_6$H$_4$Cl)}] (**4c**)*

A suitable orange crystal of the size 0.2 × 0.2 × 0.1 mm was obtained by diffusing hexane into a dichloromethane solution of **4c**. Measurements of 25 centered reflections in the range $3 < \theta < 22°$ gave a rhombohedral unit cell. Data were collected from nearly one-half of the reflection sphere in the range $7.1 < \theta < 22.5°$ (Enraf–Nonius CAD 4 diffractometer, Mo–K$_\alpha$ radiation, graphite monochromator, filter fac-

Table 2
Crystallographic data for [CpRu(dppe){$SSO_2(4\text{-}C_6H_4Cl)$}] (**4c**)

Chemical formula	$C_{37}H_{33}ClO_2P_2RuS_2$
Formula weight	772.2
Temperature (K)	193 (2)
Space group	$R\bar{3}$ (no. 148)
a (pm)	4097.6 (6)
b (pm)	4097.6 (6)
c (pm)	1153.4 (2)
V ($\times 10^{10}$ pm^3)	1.6771(5)
Z	18
λ (pm)	71.073
D_{calc} (g cm^{-3})	1.376
μ (cm^{-1})	7.20
θ Range (°)	7.1–22.5
Index range (°)	$-42 \le h \le 41$, $-41 \le k \le 41$, $-12 \le l \le -3$
Data/restraints/parameters	3236/287/406
R_1 [$I > 2\sigma(I)$]	0.0416
wR_2 [$I > 2\sigma(I)$] [a]	0.0760

[a] $wR_2 = \{[\Sigma w(F_c^2 - F_o^2)^2]/[\Sigma w(F_o^2)^2]\}^{0.5}$.

tor 15.46). Of the 8975 measured reflections, 3236 were symmetry independent (Table 2).

The structure was solved by direct methods using the program package SHELXS-97 [32] with hydrogen atoms included in their calculated positions. Refinement with the program package SHELXL-97 [33] gave the R values listed in Table 2. The highest maxima and minima of a final difference Fourier map were between 0.303 and -0.269 e Å^{-3}.

5. Supplementary material

Further details of the structure determination may be obtained from the Cambridge Crystallographic Data Centre on quoting the depository number CCDC-142352. 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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