

Partially oxidized ruthenium phosphine thiolates: [Ru(pySO₂)_{0.33}(pyS)_{1.67}(dppe)] and [Ru(pySO₂)_{0.355}(pyS)_{1.645}(dppp)]

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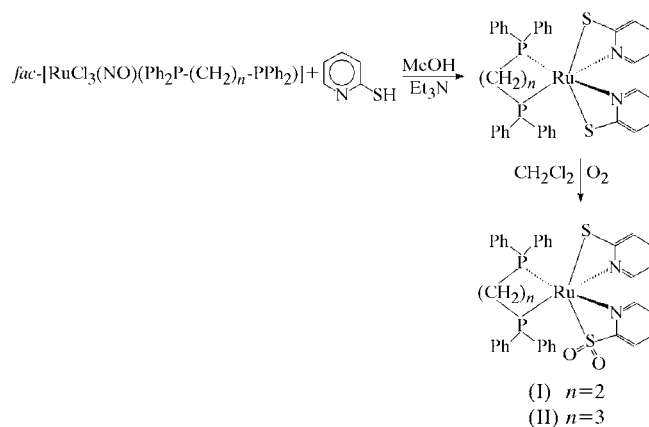
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The crystal structures of [1,3-bis(diphenylphosphino)ethane- κ^2P,P'](pyridine-2-sulfinato- κ^2N,S)(pyridine-2-thiolato- κ^2N,S)-ruthenium(II), [Ru(C₅H₄NO₂S)_{0.33}(C₅H₄NS)_{1.67}(C₂₆H₂₄P₂)] or [Ru(pySO₂)_{1-x}(pyS)_{1+x}(dppe)] ($x = 0.67$), (I), and [1,3-bis(diphenylphosphino)propane- κ^2P,P'](pyridine-2-sulfinato- κ^2N,S)(pyridine-2-thiolato- κ^2N,S)-ruthenium(II), [Ru(C₅H₄N-O₂S)_{0.355}(C₅H₄NS)_{1.645}(C₂₇H₂₆P₂)] or [Ru(pySO₂)_{1-x}(pyS)_{1+x}(dppp)] ($x = 0.645$), (II), are composed of neutral distorted octahedral Ru^{II} complexes with chelating pyridine-2-thiolate, pyridine-2-sulfinate and biphosphine ligands. The S atoms are *trans* to each other, while pairs of P and N atoms are in *cis* positions. Partial double-bond character is observed for C—S. The crystal packing consists of monolayers stabilized by C—H...O and C—H...S interactions, and is affected by the alkyl-chain lengths.

Comment

Nitric oxide (NO) is relevant for many physiological processes, such as cytotoxicity, neural transmission and blood pressure regulation, and its imbalance relates to diseases, for example, cancer, epilepsy, diabetes and arthritis (Ignarro, 2000). *S*-Nitrosothiols (*R*-SNO) are believed to play an important role in storing, transporting and releasing NO in the human body (Ignarro, 2000). The ability of transition metal complexes both to scavenge and to release NO has generated new interest in such complexes as potential metallo-pharmaceuticals (Clarke, 2003). Ruthenium has a high affinity for NO, and some complexes of this metal with coordinated NO have therapeutic use in the treatment of sepsis and in the control of high blood pressure (Clarke, 2003). The ability of {Ru(NO)}⁶ complexes, following the Enemark & Feltham (1974) notation, to form octahedral complexes is well known (Richter-Addo & Legzdins, 1992). Considering the electrophilic character of coordinated NO in a wide range of complexes, biological reducing agents, such as thiols, are able

to reduce the NO group, thus promoting its labilization (Bottomley, 1978). Against this background, it is of interest to study the reactions between nitrosyl complexes and ligands containing thiol residues, such as complexes with the general formula [Ru(SpymMe₂-*N,S*)(SpymMe₂-*S*)(NO)(P-P)]⁺ {P-P is dppe [1,2-bis(diphenylphosphino)ethane] or *c*-dppen [*cis*-1,2-bis(diphenylphosphino)ethylene] and SpymMe₂ is 2-mercapto-4,6-dimethylpyrimidine}, recently reported by some of us (Von Poelhsitz *et al.*, 2005).



Extending our previous studies, in the present work complexes with the general formula *fac*-[RuCl₃(NO)(P-P)] {P-P = dppe or dppp [1,3-bis(diphenylphosphino)propane]} were chosen as probes to evaluate the interaction between coordinated NO and the 2-mercaptopyridine (pyS⁻) ligand. The products were identified by spectroscopic techniques (³¹P NMR, IR and UV-vis) and elemental analysis as the thiolate derivatives [Ru(pyS)₂(P-P)], previously reported by Lobana *et al.* (1998) and Tiekink *et al.* (1991). In the present case, the products were obtained by the reaction shown in the scheme, while in the previously reported studies the compounds were obtained by the addition of pyS⁻ to *cis*-[RuCl₂(P-P)₂] complexes. Finally, partial oxidation of the [Ru(pyS)₂(P-P)] complexes by air produced the title compounds, (I) and (II), as expected from the well known sulfur-centred reactivity of transition metal thiolates with dioxygen to produce sulfur oxygenates (Dilworth *et al.*, 1992; Grapperhaus & Darensbourg, 1998). In the present cases, occupancy refinement showed that one S atom of each molecule was partially oxidized: the occupancies of atoms O1 and O2 (bonded to S1) refined to 0.330 (5) in (I), to give the formula [Ru(pySO₂)_{0.33}(pyS)_{1.67}(dppe)], and to 0.357 (6) in (II), to give the formula [Ru(pySO₂)_{0.36}(pyS)_{1.64}(dppp)].

The molecular structures of complexes (I) and (II) (Figs. 1 and 2) show a distorted octahedral coordination of the metal centres, with chelating pyS⁻, pySO₂⁻ and biphosphine ligands. The exocyclic S atoms occupy *trans* positions, while pairs of P and N atoms are in *cis* positions. The distortions from the ideal octahedral geometry arise from both small bite angles for pyS⁻ and pySO₂⁻ [average N—Ru—S = 67.3 (3)°] and steric crowding of the bulky biphosphine ligand. The mean Ru—P [2.279 (2) Å], Ru—N [2.139 (7) Å] and Ru—S [2.41 (3) Å] distances are in good agreement with previously reported

values for $[\text{Ru}(\text{pyS})_2(\text{P-P})]$ complexes (Lobana *et al.*, 1998; Tiekink *et al.*, 1991). The C—S bond distances [1.758 (3) and 1.731 (3) Å for (I), and 1.767 (4) and 1.744 (4) Å for (II)] suggest partial double-bond character for these bonds compared with characteristic single and double C—S bond distances (Pauling, 1960).

Two Ru/N/C/S four-membered rings are present in each complex. Ring *A* (Ru/N2/C26/S2) contains the non-oxidized S atom. Approximately one-third of rings *B* (Ru/N1/C12/S1) in the crystal of each complex contain oxidized S atoms. Geometric parameters inside rings *A* and *B* are approximately the same. Both rings are constructed by means of an Ru^{II} ion with S and N atoms from the same pyridine-2-thiolate ligand, tolerating considerable strain to achieve an octahedral coordination of Ru. As a result, the average values of the Ru—N—C [102.3 (8)°] and N—C—S [108.7(1.3)°] angles are distorted from the value of 120° expected for an sp^2 -hybridized atom. The observed Ru—S distances in the oxidized complexes (I) and (II) remain close to those observed in the non-oxidized ones.

The two S atoms are *trans* to each other, with S1—Ru1—S2 angles of 155.87 (3) and 153.87 (4)°, respectively, for (I) and (II). These angles are close to those observed in the series $[\text{Ru}(\text{pyS})_2(\text{P-P})]$, where P—P is dppe, dppp or dppb [1,4-bis(diphenylphosphino)butane], which have S—Ru—S angles in the range 153.9–155.6° (Lobana *et al.*, 1998). The P2—Ru1—P1 bite angles of 84.45 (3)° for (I) and 90.78 (5)° for (II) are related to the lengths of the alkyl chains.

The crystal packing of both compounds consists of parallel layers of molecules. The layers are stabilized by C—H...O and C—H...S interactions (Tables 2 and 4). For compound (I), these layers are parallel to the (10 $\bar{1}$) planes. The layers in compound (II) lie parallel to the (110) planes. Atom O1 is an

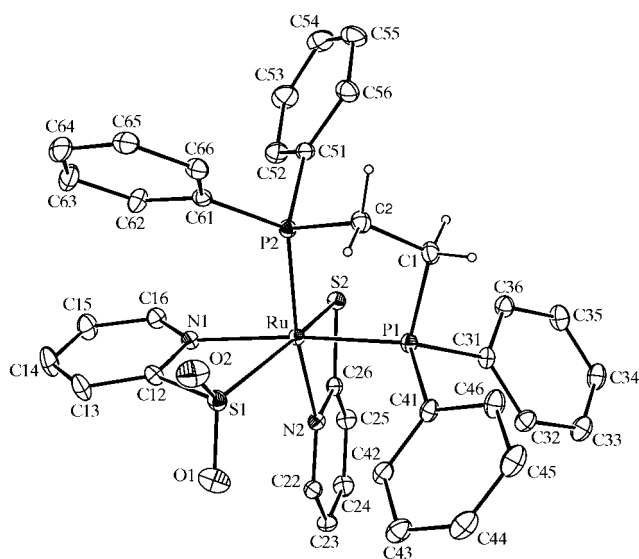


Figure 1

A structural representation of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and most H atoms have been omitted.

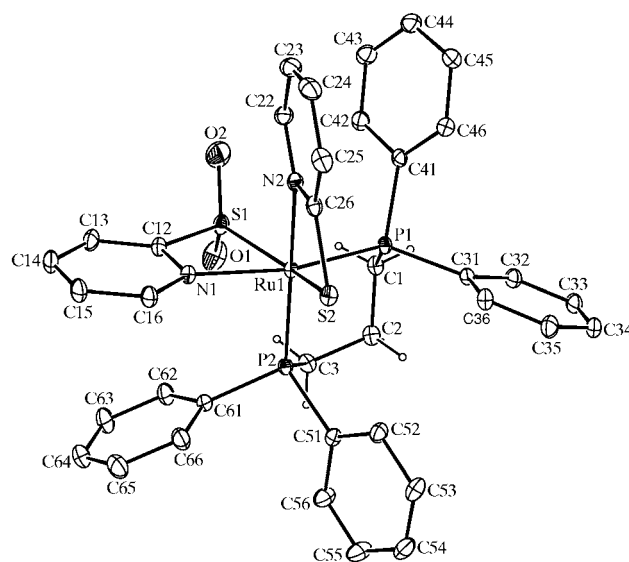


Figure 2

A structural representation of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and most H atoms have been omitted.

acceptor of one hydrogen bond in each complex. Atom O2, on the other hand, is an acceptor of two C—H...O hydrogen bonds in (I), but not in (II).

It is interesting to compare these results with the previously reported structures of the non-oxidized compounds $[\text{Ru}(\text{pyS})_2(\text{dppe})]$ (Tiekink *et al.*, 1991) and $[\text{Ru}(\text{pyS})_2(\text{dppp})]$ (Lobana *et al.*, 1998). The O atoms in the oxidized compound, (II), fill spaces that are empty in the corresponding non-oxidized structure, in such a way that isomorphism is observed between the two species. Similar to (II), compound (I) has a monolayer structure stabilized by C—H...O and C—H...S interactions. $[\text{Ru}(\text{pyS})_2(\text{dppe})]$, on the other hand, presents a double-layer structure stabilized by C—H...S interactions. Finally, it is interesting to note that the length of the alkyl groups linking the two $\text{P}(\text{Ph})_2$ units plays an important role in the crystal packing of the compounds discussed here. The packing of the complexes containing the dppp ligand (space group $P\bar{1}$ for (II) and $[\text{Ru}(\text{pyS})_2(\text{dppp})]$, isomorphous structures) is different from the packing of the crystal structures of the complexes containing the dppe ligand (space groups $P2_1/c$ and $P2_1/n$ for the crystals of the oxidized and non-oxidized species, respectively).

Experimental

A suspension of the corresponding *fac*- $[\text{RuCl}_3(\text{NO})(\text{P-P})]$ precursors (P—P is dppe or dppp) (Batista *et al.*, 1997; Zampieri *et al.*, 2002) (100 mg) in deoxygenated methanol (25 ml) was mixed with a solution of 2-mercaptopyridine (0.48 mmol, 54.0 mg) in methanol (5 ml) containing triethylamine (0.60 mmol, 0.083 ml), previously bubbled with argon for 10 min. The mixture was heated under reflux for 12 h. The resulting mixture was filtered, giving a yellow precipitate which was washed with methanol and diethyl ether, and then dried under vacuum. The same results were achieved without heating under reflux

if the time of the reaction was increased to 24 h. The [Ru(pyS)₂(P–P)] products were maintained in CH₂Cl₂ solutions and after a few days crystals of the title complexes had grown.

Compound (I)

Crystal data

[Ru(C ₅ H ₄ NO ₂ S) _{0.33} (C ₅ H ₄ NS) _{1.67} ·(C ₂₆ H ₂₄ P ₂)]	$V = 3298.9 (1) \text{ \AA}^3$
$M_r = 729.66$	$Z = 4$
Monoclinic, $P2_1/n$	$D_x = 1.481 \text{ Mg m}^{-3}$
$a = 11.4520 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 22.3900 (4) \text{ \AA}$	$\mu = 0.73 \text{ mm}^{-1}$
$c = 12.8710 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 91.661 (1)^\circ$	Prism, red
	$0.14 \times 0.10 \times 0.08 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer	80383 measured reflections
ω and φ scans	7558 independent reflections
Absorption correction: multi-scan from symmetry-related measurements (SORTAV; Blessing 1995)	5481 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.850, T_{\max} = 0.961$	$R_{\text{int}} = 0.134$
	$\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2]$
$wR(F^2) = 0.113$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{\max} = 0.001$
7558 reflections	$\Delta\rho_{\max} = 0.45 \text{ e \AA}^{-3}$
407 parameters	$\Delta\rho_{\min} = -0.83 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å) for (I).

Ru–S1	2.3977 (8)	S1–C12	1.758 (3)
Ru–S2	2.4179 (8)	P1–C1	1.844 (3)
Ru–P1	2.2785 (8)	C1–C2	1.516 (4)
Ru–P2	2.2765 (8)	C2–P2	1.835 (3)
Ru–N1	2.144 (2)	N1–C12	1.351 (4)
Ru–N2	2.141 (2)	S2–C26	1.731 (3)
S1–O1	1.470 (6)	N2–C26	1.363 (3)
S1–O2	1.346 (7)		

Table 2

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C24–H24···O2 ⁱ	0.93	2.45	3.297 (8)	152
C25–H25···O1 ⁱ	0.93	2.51	3.280 (7)	141
C65–H65···O2 ⁱⁱ	0.93	2.37	3.130 (8)	139

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + 1, -y, -z$.

Compound (II)

Crystal data

[Ru(C ₅ H ₄ NO ₂ S) _{0.355} (C ₅ H ₄ NS) _{1.645} ·(C ₂₇ H ₂₆ P ₂)]	$\gamma = 70.12 (4)^\circ$
$M_r = 745.31$	$V = 1686.7 (12) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.818 (5) \text{ \AA}$	$D_x = 1.476 \text{ Mg m}^{-3}$
$b = 10.245 (4) \text{ \AA}$	Cu $K\alpha$ radiation
$c = 20.136 (3) \text{ \AA}$	$\mu = 6.05 \text{ mm}^{-1}$
$\alpha = 83.16 (2)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 81.36 (3)^\circ$	Prism, yellow
	$0.20 \times 0.12 \times 0.09 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer	5837 independent reflections
Non-profiled $\omega/2\theta$ scans	4907 reflections with $I > 2\sigma(I)$
Absorption correction: analytical (PLATON; Spek, 2003)	$R_{\text{int}} = 0.017$
$T_{\min} = 0.42, T_{\max} = 0.64$	$\theta_{\max} = 67.0^\circ$
6012 measured reflections	1 standard reflection
	frequency: 30 min
	intensity decay: 2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.5047P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.091$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.01$	$\Delta\rho_{\max} = 0.53 \text{ e \AA}^{-3}$
5837 reflections	$\Delta\rho_{\min} = -0.65 \text{ e \AA}^{-3}$
416 parameters	
H-atom parameters constrained	

Table 3

Selected bond lengths (Å) for (II).

Ru–S1	2.3739 (12)	S1–C12	1.767 (4)
Ru–S2	2.4502 (12)	P1–C1	1.829 (3)
Ru–P1	2.2819 (16)	C2–C1	1.529 (5)
Ru–P2	2.2775 (10)	C3–C2	1.528 (5)
Ru–N1	2.141 (3)	P2–C3	1.842 (3)
Ru–N2	2.129 (3)	N1–C12	1.341 (4)
S1–O1	1.365 (8)	S2–C26	1.744 (4)
S1–O2	1.468 (8)	N2–C26	1.348 (4)

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C53–H53···O1 ⁱ	0.93	2.32	3.065 (8)	137

Symmetry code: (i) $x, y + 1, z$.

H atoms were positioned geometrically and treated as riding, with $C-H = 0.93-0.97 \text{ \AA}$ and with $U_{\text{iso}}(H) = 1.2-1.5U_{\text{eq}}(C)$.

Data collection: COLLECT (Nonius, 1999) for (I); CAD-4 EXPRESS (Enraf–Nonius, 1994) for (II). Cell refinement: SCALEPACK (Otwinowski & Minor, 1997) for (I); CAD-4 EXPRESS for (II). Data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK for (I); XCAD4 (Harms & Wocadlo, 1995) for (II). For both compounds, program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3001). Services for accessing these data are described at the back of the journal.

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