syn-Tetracarbonyldi-μ-phenylthiolato-bis[(triphenylphosphine)ruthenium(I)]

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Key indicators

The title *syn* isomer of [Ru$_2$(μ-SPh)$_2$(PPh$_3$)$_2$(CO)$_4$] or [Ru$_2$(μ-C$_6$H$_5$S)$_2$(C$_{18}$H$_{15}$P)$_2$(CO)$_4$], which was previously expected to be present in solution, is now confirmed by the determination of its crystal structure. The compound contains two six-coordinated Ru^I atoms, joined by an Ru—Ru single bond with a length of 2.6809 (6) Å. A mirror plane passes through the mid-point of the Ru—Ru bond and the two bridging thiolate ligands.

Comment

In recent years, extensive research has been carried out on transition-metal complexes with sulfur ligands. These complexes often display unusual structures and novel reactivity (Stiefel, 1996), and show some relevance to metal sulfide hydrodesulfurization and demercuration catalysts (Angelici, 1988; Wiegand & Friend, 1992). Based on NMR evidence reported previously (Shiu *et al.*, 1998), both *syn*, (I), and *anti*, (II), isomers of [Ru$_2$(μ-SPh)$_2$(PPh$_3$)$_2$(CO)$_4$] are believed to be present in an equilibrium mixture in solution, but with one crystal structure determined for the *anti* form as the major component. In order to further confirm the presence of the *syn* isomer and compare the structure details of the two isomers, single crystals of the minor *syn* isomer were prepared and its crystal structure characterized by X-ray crystallography.

(I)
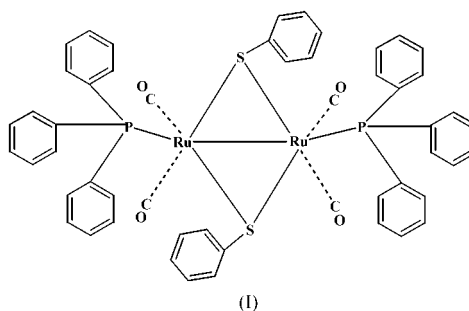
The single crystals of (I) are orthorhombic, while those of (II) are triclinic. The structure of (I) is composed of discrete monomers with no short intermolecular interactions. A view of the molecular structure is shown in Fig. 1. This structure contains a crystallographically imposed mirror plane containing the mid-point of the Ru—Ru bond, two S atoms, and eight C atoms, *viz*. C3 and C6–C12. A projection view of (I) along the Ru1→Ru1′ vector (Fig. 2) confirms that it is the *syn* rather than the *anti* form (Shiu *et al.*, 1998). The Ru—Ru, Ru—P, Ru—S and Ru—CO bond lengths, and all other bond lengths (Table 1), are similar to those observed in the *anti* isomer (II). However, the non-bonded distances, such as P···P and S···P, are quite different in the two isomers [P···P =
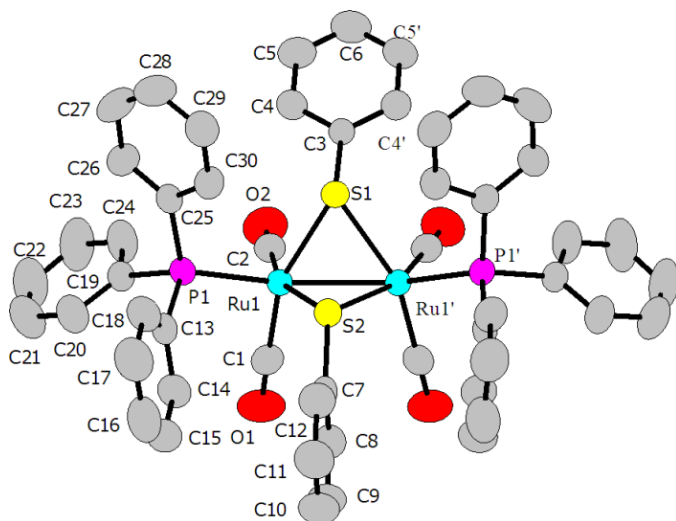
Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. The prime in atom names corresponds to symmetry code (i) in Table 1.

6.782 Å in (I) *versus* 7.110 Å in (II) and S···S = 2.863 Å in (I) *versus* 3.101 Å in (II)]. Likewise, most angles are different in the two structures. These different features probably reflect the different influences caused by the different second-sphere face-to-face π–π stacking interactions (Shiu *et al.*, 2002). Although each thiolate phenyl group interacts in this way with its own specific partner phenyl of one PPh₃ ligand in (II) (Shiu *et al.*, 1998), only one thiolate phenyl group, C7—C12, interacts similarly with two PPh₃ phenyl groups, C13—C18 and C13′—C18′ in (I) (Fig. 1). This thiolate phenyl group is sandwiched between two almost parallel phenyl planes of PPh₃ with close contacts of 3.45–4.03 Å.

Experimental

Both (I) and (II) were obtained as a mixture by following the published procedure (Shiu *et al.*, 1998). Single crystals of both isomers were grown from CH_2Cl_2/hexane (1:4) at ambient temperature. Two types of crystals, irregular chunks and cylinders, were found with a microscope. The former type are the *anti* isomer, whereas the latter are the expected *syn* isomer.

Crystal data

$[Ru_2(C_6H_5S)_2(C_{18}H_{15}P)_2(CO)_4]$	Mo $K\alpha$ radiation
$M_r = 1057.04$	Cell parameters from 3928
Orthorhombic, $Pnma$	reflections
$a = 17.2502 (9)$ Å	$\theta = 2.5$–25°
$b = 24.4253 (13)$ Å	$\mu = 0.83$ mm^{-1}
$c = 11.3154 (6)$ Å	$T = 294 (2)$ K
$V = 4767.6 (4)$ Å^3	Column, yellow
$Z = 4$	$0.30 \times 0.11 \times 0.10$ mm
$D_x = 1.473$ Mg m^{-3}	

Data collection

Siemens SMART CCD area-detector diffractometer	5947 independent reflections
φ and ω scans	3016 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1995)	$R_{int} = 0.106$
	$\theta_{max} = 28.3°$
$T_{min} = 0.818$, $T_{max} = 0.922$	$h = -22 \rightarrow 22$
29 562 measured reflections	$k = -18 \rightarrow 32$
	$l = -15 \rightarrow 14$
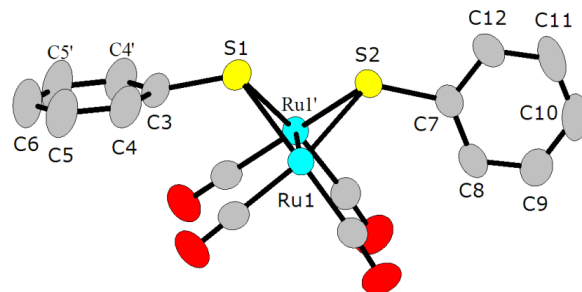
Figure 2
A projection of (I) along the Ru1→ Ru1′ vector. The two PPh₃ groups have been omitted for clarity.

Refinement

Refinement on F^2	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2]$
$wR(F^2) = 0.069$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.88$	$(\Delta/\sigma)_{max} = 0.002$
5947 reflections	$\Delta\rho_{max} = 0.81$ e Å^{-3}
295 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—C2	1.858 (4)	Ru1—Ru1^i	2.6809 (6)
Ru1—C1	1.866 (4)	S1—C3	1.782 (5)
Ru1—P1	2.3713 (10)	S2—C7	1.788 (5)
Ru1—S2	2.4294 (11)	O1—C1	1.145 (4)
Ru1—S1	2.4428 (11)	O2—C2	1.145 (4)
C2—Ru1—C1	88.99 (16)	S1—Ru1—Ru1^i	56.720 (18)
S2—Ru1—S1	71.98 (4)	O1—C1—Ru1	176.0 (4)
P1—Ru1—Ru1^i	149.85 (2)	O2—C2—Ru1	178.2 (4)
S2—Ru1—Ru1^i	56.513 (17)		

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

The H atoms were located in a difference Fourier synthesis but were not refined; their U_{iso} values were set to 0.08 Å^2.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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