

Tetrakis(pentafluorobenzenethiolato- κ S)(triphenylphosphine- κ P)-osmium(IV): a $Z' = 3$ structure with a supramolecular double-stranded backbone

Consuelo Mendoza, Sylvain Bernès*‡ and Maribel Arroyo

Centro de Química del Instituto de Ciencias, BUAP, Puebla, Pue., Mexico
Correspondence e-mail: sylvain_bernes@hotmail.com

Received 3 February 2006

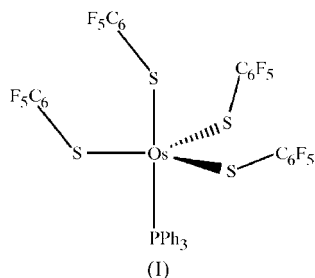
Accepted 29 March 2006

Online 13 April 2006

The title complex, $[\text{Os}(\text{C}_6\text{F}_5\text{S})_4(\text{C}_{18}\text{H}_{15}\text{P})]$, crystallizes with three independent molecules in the asymmetric unit. Two of these have very similar conformations, while in the third, the axial thiolate ligand has a rotation that differs by *ca* 21.5° . The coordination around the metal atom is trigonal bipyramidal and the supramolecular structure involves an unusual double-stranded backbone.

Comment

Owing to their ability to coordinate to almost every transition metal, tertiary phosphines, PR_3 , are widely used for the preparation of stable organometallic complexes. Within this class of ligands, triphenylphosphine is one of the most commonly used (Crabtree, 2001); for example, it is used for



stabilizing 16-electron complexes such as Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ or Vaska's catalyst $[\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2]$. Approximately 9000 PPh_3 -containing transition metal complexes appear in the Cambridge Structural Database, in 430 of which the metal centre is osmium (CSD; Version 5.27; Allen, 2002). The title compound, (I), was crystallized as part of a long-standing project involving mononuclear Os-based complexes of a variety of thiolate and phosphine ligands. Although this air-stable complex has been available as single

‡ Present address: DEP Facultad de Ciencias Químicas, UANL, Guerrero y Progreso S/N, Col. Treviño, 64570 Monterrey, NL, Mexico.

crystals for a decade, X-ray data had never been measured, since the formula and coordination geometry were available from analytical data and by analogy with a structurally characterized complex containing $\text{SC}_6\text{F}_4\text{H}$ thiolate functionalities in place of SC_6F_5 (Arroyo *et al.*, 1994).

The asymmetric unit of (I) contains three independent molecules of $[\text{Os}(\text{SC}_6\text{F}_5)_4(\text{PPh}_3)]$ in general positions, with no evidence of pseudo- or non-crystallographic symmetry. In each molecule (denoted *A*, *B* and *C* hereinafter; see Figs. 1, 2 and 3, respectively), the metal centre displays a trigonal-bipyramidal coordination geometry very similar to that found in the closely related complex $[\text{Os}(\text{SC}_6\text{F}_4\text{H})_4(\text{PPh}_3)]$ (Arroyo *et al.*, 1994). This geometry has also been observed in a number of Os^{IV} complexes of general formula $[\text{Os}(\text{SR}')_4(\text{PR}_3)]$, where PR_3 is a *para*-substituted tertiary phosphine and the SR' groups are fluorinated thiolates (Mendoza *et al.*, 2006). The axial positions in (I) are occupied by mutually *trans* thiolate and triphenylphosphine ligands [$\text{S}-\text{Os}-\text{P} = 173.81(9)-176.85(9)^\circ$], while the remaining three equatorial positions are occupied by three thiolate ligands. For obvious steric reasons (Fig. 1), the pentafluorophenyl rings of the equatorial ligands are directed away from the axial phosphine ligand. The $\text{P}-\text{C}_{\text{ipso}}$ bonds are staggered with respect to the equatorial $\text{Os}-\text{S}$ bonds; such an arrangement probably minimizes the overall steric hindrance in the whole molecule. Other bond lengths and angles in (I) are within normal ranges and no unexpected features were detected.

A least-squares fit between the OsS_4P coordination environments of the three independent molecules in (I) shows that

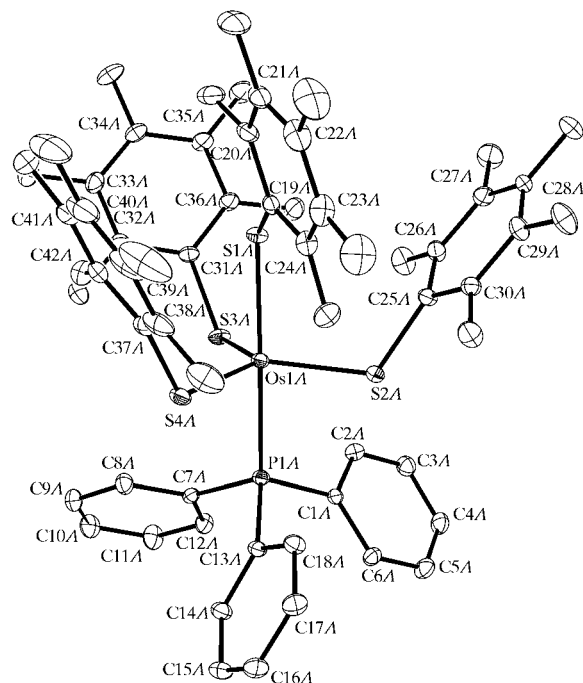


Figure 1
A view of molecule *A* in the asymmetric unit of (I), with displacement ellipsoids drawn at the 10% probability level. H atoms have been omitted for clarity. The labelling scheme is given for non-F atoms. F atoms are labelled as their carrier C atoms.

the geometry for this core is constant (the r.m.s. deviations for each pair of molecules are 0.048 Å for *A/B* and 0.035 Å for both *B/C* and *A/C*). However, consideration of the entire molecules clearly shows that two rotamers are present in the solid state (Fig. 4); while molecules *B* and *C* match very well, the axial thiolate ligand in molecule *A* is rotated by *ca* 21.5° relative to those in molecules *B* and *C*. From the positions of the axial thiolate groups in both rotamers, it can be seen that the observed rotational isomerism is due to a non-restricted rotation about Os—S_{axial} and S_{axial}—C_{ipso} σ bonds, which is reflected in the S_{equatorial}—Os—S_{axial}—C_{ipso} torsion angles (Table 1). The *Z'* ≠ 1 value obtained for (I) may also be connected to a limited libration of the terminal thiolate groups, affecting above all the functional group bonded to atom S3 (Fig. 4). Complex (I) is thus found in the solid state as a 1:2 mixture of rotamers. Some related cases of organometallic cocrystals have been described; for example, two rotamers of a palladium maleic anhydride complex have been observed in a single crystal (Gómez-de la Torre *et al.*, 1998). A remarkable example has also been described for [PtCl₂(quinoline)₂], which crystallizes as a 1:1 mixture of head-to-head and head-to-tail conformers (Davies *et al.*, 2001). The extensive work described in that paper showed that in dimethylformamide solution these conformers also interconvert by rotation about a Pt—N bond. In the case of (I), no evidence has so far been found to support an interconversion mechanism in solution, and the minor differences in conformation in the solid state may be a consequence of crystal packing forces.

Crystal structures with *Z'* > 1 can pose experimental problems, as the molecules in these crystals may be not

densely packed, giving poorly diffracting samples (Lehmler *et al.*, 2002) or low-melting materials (McCourt *et al.*, 1996). However, this is not the case for (I), where the packing index (Spek, 2003) of 0.664 falls in the normal range for organometallic compounds and the density of 1.898 Mg m⁻³ is comparable to the value of 1.846 Mg m⁻³ observed for the *Z'* = 1 complex [Os(SC₆F₄H)₄(PPh₃)] (Arroyo *et al.*, 1994). In (I), molecules are well packed at van der Waals distances, leaving no significant voids (Spek, 2003). This efficient packing could

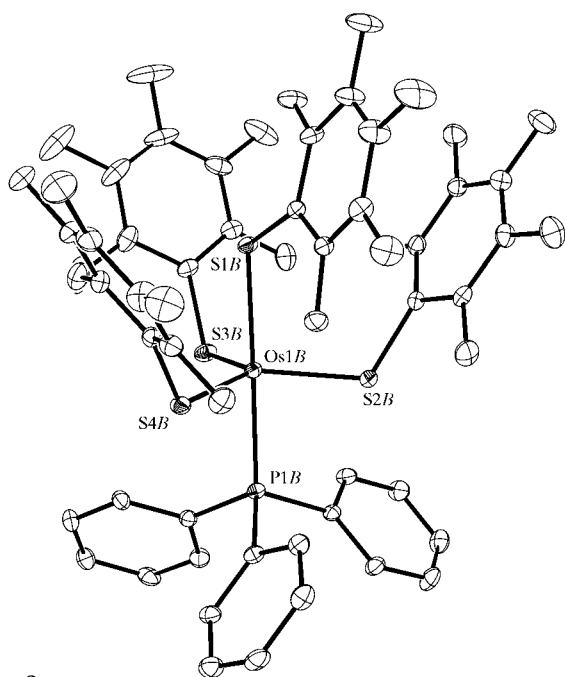


Figure 2
A view of molecule *B*, with displacement ellipsoids drawn at the 10% probability level. H atoms have been omitted and the numbering scheme is analogous to that adopted for molecule *A* (Fig. 1), substituting suffix '*B*' for suffix '*A*'.

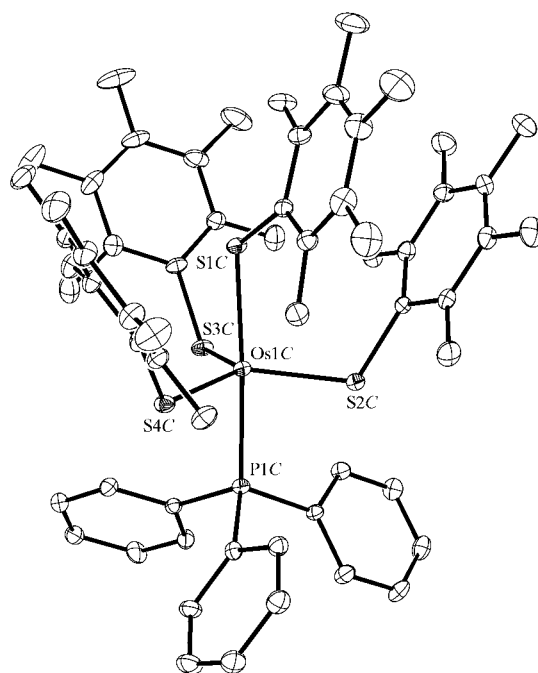


Figure 3
A view of molecule *C*, with displacement ellipsoids drawn at the 10% probability level. H atoms have been omitted and the numbering scheme is analogous to that adopted for molecule *A* (Fig. 1), substituting suffix '*C*' for suffix '*A*'.

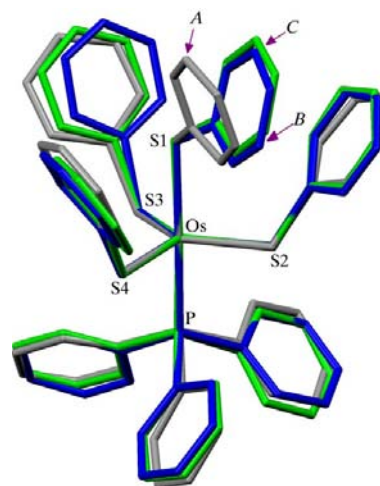


Figure 4
An overlay of the three non-symmetry-related molecules present in the solid state for (I). The fit has been carried out on Os, S and P atoms by using the overlay facility of *MERCURY* (Version 1.4.1; Bruno *et al.*, 2002).

be related to the near-globular shape of the molecule, and the fact that the F atoms are relegated to one half of the coordination sphere, while the other hemisphere, occupied by the PPh₃ ligand, contains only C and H atoms. This arrangement results in polar molecules which can pack according to essentially electrostatic forces.

The centroid of the asymmetric unit computed using all the atoms in the three independent molecules lies at (0.581, 0.571, 0.179), close to the 2₁ screw axis at ($\frac{1}{2}$, y , $\frac{1}{4}$). As a consequence, the array of three molecules forms a zigzag chain running along the *b* axis (Fig. 5), its period of $b/3 \simeq 14.9$ Å being imposed by symmetry. Owing to the mutually *trans* arrangement of the F-containing SC₆F₅ ligands and the H-containing PPh₃ ligand within the coordination sphere, the supramolecular structure of (I) is based on an unusual double-stranded backbone running parallel to the *b* axis. One strand contains all F atoms, while the second strand, embedded with the first one, contains C and H atoms of the PPh₃ ligands. This supramolecular association of asymmetric units in (I) is reflected in the anisotropy of the unit cell, with a *b/a* ratio close to 3.5.

Work is now underway to characterize (I) in solution, mainly using variable-temperature ¹⁹F NMR experiments. The current *Z'* = 3 complex is unique within the closely analogous series of [Os(SR')₄(PR₃)] complexes we have synthesized over a decade (Abasq *et al.*, 1996; Arroyo *et al.*, 2000; Mendoza *et al.*, 2006), which otherwise crystallize with *Z'* = 1. Therefore, it would not be surprising if a structure with *Z'* = 1 were subsequently identified for the title complex, perhaps by varying the experimental conditions used for crystal growth.

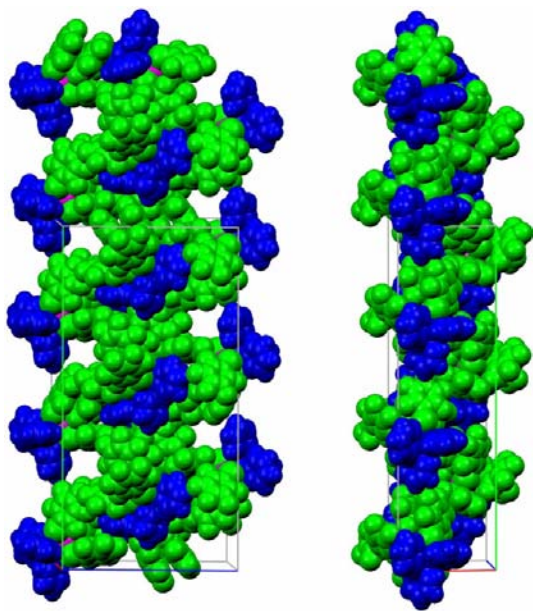


Figure 5

Part of the packing structure of (I), in a CPK space-filling representation (Bruno *et al.*, 2002), viewed down [100] (left) and down [001] (right). The vertical axis corresponds to the *b* cell axis in both views. Lighter coloured atoms identify the hemisphere containing fluorinated thiolate groups, whereas darker atoms identify the hemisphere with the C and H atoms of the PPh₃ ligands.

Experimental

The title compound was prepared following a published procedure (Arroyo *et al.*, 1994) in *ca* 87% yield, and was crystallized by slow evaporation from a hexane–dichloromethane (3:2) solution at 298 K.

Crystal data

[Os(C ₆ F ₅ S) ₄ (C ₁₈ H ₁₅ P)]	<i>Z</i> = 12
<i>M_r</i> = 1248.95	<i>D_x</i> = 1.898 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 13.0394 (13) Å	<i>μ</i> = 3.26 mm ⁻¹
<i>b</i> = 44.781 (3) Å	<i>T</i> = 299 (2) K
<i>c</i> = 22.8023 (17) Å	Tabular prism, dark green
<i>β</i> = 100.051 (8)°	0.4 × 0.2 × 0.2 mm
<i>V</i> = 13110.4 (19) Å ³	

Data collection

Bruker <i>P4</i> diffractometer	15318 reflections with <i>I</i> > 2σ(<i>I</i>)
2θ/ω scans	<i>R</i> _{int} = 0.045
Absorption correction: ψ scan	<i>θ</i> _{max} = 25.0°
(<i>XSCANS</i> ; Siemens, 1996)	3 standard reflections
<i>T</i> _{min} = 0.362, <i>T</i> _{max} = 0.521	every 97 reflections
27759 measured reflections	intensity decay: 3.5%
22988 independent reflections	

Refinement

Refinement on <i>F</i> ²	(Δ/σ) _{max} = 0.002
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.055	Δρ _{max} = 1.56 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.144	Δρ _{min} = -1.84 e Å ⁻³
<i>S</i> = 1.01	Extinction correction:
22988 reflections	<i>SHELXTL-Plus</i>
1838 parameters	Extinction coefficient:
H-atom parameters constrained	0.000195 (12)
<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0398 <i>P</i>) ²	
+ 114.1882 <i>P</i>]	
where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3	

Table 1

Selected torsion angles (°).

S2A–Os1A–S1A–C19A	–73.1 (3)	S4B–Os1B–S1B–C19B	74.2 (4)
S3A–Os1A–S1A–C19A	168.7 (3)	S2C–Os1C–S1C–C19C	–47.1 (4)
S4A–Os1A–S1A–C19A	52.2 (3)	S3C–Os1C–S1C–C19C	–164.5 (4)
S2B–Os1B–S1B–C19B	–53.1 (4)	S4C–Os1C–S1C–C19C	78.7 (4)
S3B–Os1B–S1B–C19B	–169.2 (4)		

The structure was refined (Sheldrick, 1998) using a least-squares matrix partitioned into three blocks, each containing positional and displacement parameters for a single molecule. H atoms were placed in idealized positions and refined using a riding-model approximation (C–H = 0.93 Å) and fixed isotropic displacement parameters [*U*_{iso}(H) = 1.2*U*_{eq}(C)]. In order to obtain a sensible geometry for the PPh₃ and SC₆F₅ ligands, the C atoms of each ring were restrained to lie in a common plane (chiral volumes defined by tetrahedra restrained to zero with a standard deviation of 0.1 Å³) and twofold symmetry was applied to six-membered rings, within a standard deviation of 0.02 Å. Similarity restraints were applied, with a 0.02 Å standard deviation, for all C₆H₅ or C₆F₅ units in each independent molecule. Finally, rigid bond restraints were applied for all C–C bonds in these ligands; the components of the anisotropic displacement parameters in the direction of each bond were restrained to be equal within an effective standard deviation of 0.01 Å². In the last cycles, a set of 20 reflections with *F*_o >> *F*_c was omitted, yielding slightly better residual parameters. The highest peak and deepest hole in the difference Fourier synthesis, which lie, respectively, 0.84 and 0.91 Å from atom Os1A, may result from limitations in the

absorption corrections applied and have no chemical significance. Displacement parameters for F atoms [U_{eq} range = 0.0692 (17)–0.224 (8) Å²] are significantly higher than those of their carrier C atoms [U_{eq} range = 0.046 (2)–0.157 (8) Å²]. However, this is a feature found in the majority of perfluorinated compounds.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus* and *MERCURY* (Version 1.4.1; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL-Plus*.

The authors are grateful to CONACyT (grant No. 27915-E) and VIEP-UAP (grant No. 2/G/NAT/05) for financial support. SB is grateful to an anonymous referee for identifying a misinterpretation of overlaid molecules in centrosymmetric space groups.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1627). Services for accessing these data are described at the back of the journal.

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