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MONOTHIOCARBOXYLATE COMPLEXES OF OSMIUM(III) WITH FLUORO-THIOLATES AND DIMETHYLPHENYLPHOSPHINE CO-LIGANDS. X-RAY CRYSTAL STRUCTURES OF $[Os(SR)_2(SOCCH_3)(PMe_2Ph)_2]$ $(R = C_6F_5$ OR $C_6F_4H\text{-}4)$

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Abstract—Treatment of the pentacoordinated complexes $[Os(SR)_3(PMe_2Ph)_2]$ $(R = C_6F_5$ or $C_6F_4H\text{-}4)$ with R′COSH $(R' = CH_3$ or $C_6H_5)$ in acetone gave the blue paramagnetic osmium(III) derivatives $[Os(SC_6F_5)_2(SOCR')(PMe_2Ph)_2]$ (**1**) and $[Os(SC_6F_4H\text{-}4)_2(SOCR')(PMe_2Ph)_2]$ (**2**). Mass spectrometric data are given. X-ray crystallography has shown that **1** $(R' = CH_3)$ and **2** $(R' = CH_3)$ have an octahedral structure with *trans*-thiolates, *cis*-phosphines and a chelating monothioacetate ligand. The electrochemical reduction of these compounds was studied by cyclic voltammetry in DMF. The potential at which the compounds undergo reduction was found to be nearly independent of the nature of the substituent group on the monothiocarboxylate ligand and slightly more dependent on the identity of the substituent group on the thiolate ligands, the reduction becoming easier for the more electron-withdrawing thiolate derivatives.

The chemistry of the thiolate ligands has afforded interesting examples of unusual coordination geometries and also a variety of interesting steric and electronic properties for their transition metal derivatives.[1–5] The chemistry of iron-group metals with sulphur-donor ligands has aroused great interest since it could be relevant to several biological and catalytic systems. Yet the chemistry of monothiocarboxylates of osmium has remained practically unexplored until very recently.[6]

Previously we have reported the synthesis and structural characterization of $[Os(SR)_2(O_2CPh)(PMe_2Ph)_2]$ $(R = C_6F_5$ or $C_6F_4H\text{-}4)$.[7] As an extension of this work we here report a similar study on $[Os(SR)_2(SOCR')(PMe_2Ph)_2]$ $(R = C_6F_5$ or $C_6F_4H\text{-}4$, $R' = CH_3$ or $C_6H_5)$.

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EXPERIMENTAL

IR spectra were obtained using a Perkin–Elmer FTIR-1600 instrument. Elemental analyses were by Galbraith Laboratories Inc. Magnetic data were determined at room temperature using Gouy's method on a recording Johnson Matthey magnetic balance. FAB mass spectrometry molecular weights were determined on an MS-Varian instrument with 3-nitrobenzylamine as matrix at the UAM, Madrid, Spain. Cyclic voltammetry was performed on a BAS 100A electrochemical analyser. The working electrode was a platinum electrode. An Ag/AgCl saturated electrode was used as reference and a platinum wire as an auxiliary electrode. Solutions contained 10^{-3} mol dm^{-3} of complex and 0.1 mol dm^{-3} of $NBu^n_4PF_5$.

Since all complexes proved to be stable to air, reactions were carried out on open systems and at room temperature.

The monothiocarboxylic acids were from Aldrich Chem. Co. whereas $[Os(SR)_3(PMe_3Ph)_2]$ were prepared as published.[7]

Preparations

The general method is described only for the case of $[Os(SC_6F_5)_2(OSCMe)(PMe_2Ph)_2]$ (**1a**). To $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ (0.2 mmol) dissolved in acetone (40 cm^3) was added MeCOSH (0.3 mmol). Immediately the solution changed from purple to dark blue. The solution was stirred at room temperature for *ca* 2 h. The resulting solution was evaporated to dryness under reduced pressure to give a blue solid which was washed with cold ethanol and recrystallized from acetone–ethanol solution. **1a**. Yield 85%; m.p. 203–207°C (decomp.); μ_{eff} 2.03 B.M. (Found: C, 37.9; H, 2.6; S, 9.9. $C_{30}H_{25}F_{10}OOsP_2S_3$ requires C, 38.3; H, 2.7; S, 10.2%). **1b**. Yield 95%; m.p. 190–194°C (decomp.); μ_{eff} 1.89 B.M. (Found: C 42.6; H, 3.0; S, 9.4. $C_{35}H_{27}F_{10}OOsP_2S_3$ requires C, 42.0; H, 2.7; S, 9.6%). **2a.** Yield 70%; m.p. 229–232°C (decomp.); μ_{eff} 1.91 B.M. (Found: C, 39.6; H. 3.0; S, 10.6. $C_{30}H_{27}F_8OOsP_2S_3$ requires C, 39.9; H, 3.0; S, 10.6%). **2b**. Yield 85%; m.p. 156–160°C; μ_{eff} 2.07 B.M. (Found: C, 43.6; H, 3.1; S, 9.9. $C_{35}H_{29}F_8OOsP_2S_3$ requires C, 43.5; H, 3.0; S, 10.0%).

X-ray crystal structure of 1 (R′ = Me): $[Os(SC_6F_5)_2(OSCMe)(PMe_2Ph)_2]$

Crystal data. $C_{30}H_{25}F_{10}OOsP_2S_3$, $M = 939.82$, triclinic, $a = 11.340(1)$, $b = 17.541(2)$, $c = 18.236(3)$ Å, $\alpha = 77.91(1)$, $\beta = 79.60(1)$, $\gamma = 80.960(7)$°, $U = 3461.7(8)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), space group $P\bar{1}$ (no. 2), $Z = 4$, $D_c = 1.803$ g cm^{-3}, $F(000) = 1828$. Dark blue monocrystals. Crystal size $= 0.31 \times 0.23 \times 0.08$ mm, $\mu(\text{Mo-}K_\alpha) = 4.035$ mm^{-1}, $T = 293(2)$ K.

Data collection and processing. CAD4 diffractometer $\omega/1.66\theta$ mode with ω scan width $= 0.80 + 0.34 \tan\theta$, ω scan speed 1.3–5.5° min^{-1}, graphite-monochromated Mo-K_α radiation; 21 545 reflections were collected; 20 924 independent. Psi-scan absorption correction (max., min. transmission: 0.99, 0.67) giving 11 091 with $I > 2\sigma(I)$, 20 921 θ used for refinement range for data collection: 2.31–30.42°, index ranges; $-15 \leqslant h \leqslant 16, 0 \leqslant k \leqslant 24, -25 \leqslant l \leqslant 25$.

Structure analysis and refinement. Direct methods[8] (most atoms) followed by difference Fourier synthesis. Full-matrix least-squares refinement[9] on F^2 with all non-hydrogen atoms anisotropic. The phenyl rings have been treated as rigid units and the hydrogen atoms placed at calculated positions. The weighting scheme $w = 1/[\sigma^2(F^2_o) + (0.391P)^2 + 2.44P]$ where $P = [\text{Max}(F^2_o) + 2F^2_c]/3$. Final R indices $[I \geqslant 2\sigma(I)]$ are $R_1 = 0.0373$, $wR_2 = 0.0758$, and R indices, with all data, $R_1 = 0.1553$, $wR_2 = 0.1031$. Values of electron density synthesis with coefficients $F_o - F_c$: max. 0.95 min. -2.44 eÅ^{-3}. Goodness-of-fit = 1.01. Source of scattering factors and f', f'', Ref. 10. Atomic coordinates, thermal parameters and observed and calculated structure factors are available as supplementary material.

X-ray crystal structure of 2 (R′ = Me): $[Os(SC_6F_4H\text{-}4)_2(OSCMe)(PMe_2Ph)_2]$

Crystal data. $C_{30}H_{27}F_8OOsP_2S_3$, $M = 903.84$, triclinic, $a = 11.195(2)$, $b = 17.297(2)$, $c = 18.283(2)$ Å, $\alpha = 77.49(1)$, $\beta = 79.98(1)$, $\gamma = 81.82(1)$°, $U = 3383$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), space group $P\bar{1}$ (no. 2), $Z = 4$, $D_c = 1.774$ g cm^{-3}, $F(000) = 1764$. Dark blue monocrystals. Crystal size $= 0.40 \times 0.35 \times 0.22$ mm, $\mu(\text{Mo-}K_\alpha) = 4.117$ mm^{-1}, $T = 293(2)$K.

Data collection and processing. CAD4 diffractometer $\omega/1.66\theta$ mode with ω scan width $= 0.80 + 0.34 \tan\theta$, ω scan speed 1.3–5.5° min^{-1}, graphite-monochromated Mo-K_α radiation; 10 357 reflections were collected; 9991 independent. Psi-scan absorption correction (max., min. transmission: 99.9 and 60.9) giving 8664 with $I > 2\sigma(I)$. θ range for data collection: 1.15–23.47°, index

Table 1. Physical properties of osmium complexes

Compound	Yield (%)	M.p. (°C)	μ_{eff} (B.M.)	Mass (molecular ion)[a,c] m/z	IR (cm^{-1})[d]
$[Os(SC_6F_5)_2(OSCMe)(PMe_2Ph)_2]$ (**1a**)	85	203–207[b]	2.03	940.9 (941.0)	1500, 1480, 974, 848 1300, 1284, 492
$[Os(SC_6F_5)_2(OSCPh)(PMe_2Ph)_2]$ (**1b**)	95	190–194[b]	1.89	1002.9 (1003.0)	1500, 1478, 974, 848 1310, 1300, 490
$[Os(SC_6HF_4)_2(OSCMe)(PMe_2Ph)_2]$ (**2a**)	70	229–232[b]	1.91	905.0 (905.0)	1482, 1222, 1178, 908 1300, 1280, 492
$[Os(SC_6HF_4)_2(OSCPh)(PMe_2Ph)_2]$ (**2b**)	85	156–160	2.07	967.0 (967.0)	1480, 1222, 1170, 908 1310, 1300, 490

[a] Calculated values in parentheses.

[b] With decomposition.

[c] Determined by FAB mass spectrometry.

[d] Selected bands only, KBr discs.

ranges: $-12 \leqslant h \leqslant 12$, $-18 \leqslant k \leqslant 19$ and $0 \leqslant l \leqslant 20$.

Structure analysis and refinement. Direct methods[8] (most atoms) followed by difference Fourier synthesis. Full-matrix least-squares refinement[9] on F^2 with all non-hydrogen atoms anisotropic. The phenyl rings have been treated as rigid units. All the hydrogen atoms were located on the difference Fourier map. The weighting scheme $w = 1/[\sigma^2(F_o^2(+ (0.326P)^2 + 6.81P]$ where $P = [\mathrm{Max}(F_o^2) + 2F_c^2]/3$. Final R indices $[I \geqslant 2\sigma(I)]$ are $R_1 = 0.0235$, $wR_2 = 0.0565$, and R indices, with all data: $R_1 = 0.0329$, $wR_2 = 0.0607$. Values of electron density synthesis with coefficients F_o-F_c: max. 1.15, min. -0.83 eÅ^{-3}. Goodness-of-fit = 0.98. Source of scattering factors and f', f'', Ref. 10. Atomic coordinates, thermal parameters and observed and calculated structure factors are available as supplementary material.

RESULTS AND DISCUSSION

The compounds $[Os(SR)_2(O_2CPh)(PMe_2Ph)_2]$ ($R = C_6F_5$ or C_6F_4H-4) have been previously prepared[7] by reactions of $C_6H_5CO_2H$ with $[Os(SR)_3(PMe_2Ph)_2]$. We have now prepared the related monothiocarboxylate complexes by reaction of the same unsaturated osmium(III) thiolates $[Os(SR)_3(PMe_2Ph)_2]$ with monothiocarboxylic acids R′COSH ($R' = CH_3$ and C_6H_5) in acetone at room temperature. These reactions yielded the compounds $[Os(SC_6F_5)_2(SOCR')(PMe_2Ph)_2]$, **1** and $[Os(SC_6F_4H\text{-}4)_2(SOCR')(PMe_2Ph)_2]$, **2**, with thiolate displacement according to Scheme 1.

$$[Os(SR)_3(PMe_2Ph)_2)] + R'COSH \longrightarrow [Os(SR)_2(SOCR')(PMe_2Ph)_2] + RSH$$

Scheme 1.

All monothiocarboxylate complexes were obtained as stable, blue crystalline solids, with μ_{eff} values on the range expected for paramagnetic osmium(III) species.

Analysis, IR spectroscopy and details of physical properties for compounds **1** and **2** are given in Table 1.

IR spectra of complexes **1** and **2** show the expected bands for SC_6F_5 or SC_6F_4H-4 and PMe_2Ph ligands. IR spectroscopy is successfully used to decide between the possible coordination modes of the monothiocarboxylate skeleton.[11] Unfortunately the bands expected for the moiety S—C—O in complexes **1** and **2** overlap with absorptions arising from other ligands precluding such distinction. Nevertheless the absence of absorptions attributable to the double bond (C=O) vibrations seems to indicate that oxygen co-ordination is present in complexes **1** and **2**.

Mass spectra

Mass spectrometric data from FAB mass spectrometry for compounds **1** and **2** show molecular ion signals. High or considerable intensities are found for ions resulting from the loss of one thiolate ligand and for ions resulting from the loss of the one phosphine ligand. Low intensities are found for the signals of ions resulting from the loss of the monothioacetate ligand and considerable intensities

Table 2. Cyclic voltammetry data for $[Os(SR)_2(SOCR')(PMe_2Ph)_2]$ complexes[a]

Compound	$E_{1/2}$, V	(ΔE, mV)
$[Os(Sc_6F_5)_2(SOCCH_3)(PMe_2Ph)_2]$	−0.450	(86)
$[Os(SC_6F_5)_2(SOCC_6H_5)(PMe_2Ph)_2]$	−0.452	(83)
$[Os(SC_6F_4H\text{-}4)_2(SOCCH_3)(PMe_2Ph)_2]$	−0.504	(88)
$[Os(SC_6F_4H\text{-}4)_2(SOCC_6H_5)(PMe_2Ph)_2]$	−0.517	(96)

[a] $E_{1/2}$ = half-wave potential, ΔE = peak separations between anodic and cathodic peaks of cyclic voltammograms. All potentials measured at scan rate = 0.050 V s^{-1} using $NBu^n_4PF_6$ (0.1 mol dm^{-3}) as supporting electrolyte in DMF and complex concentration 10^{-3} mol dm^{-3}.

for the ions resulting from the loss of the monothiobenzoate ligand. The intensities of corresponding signals to $C_6H_5CO^+$ ions are much stronger than those corresponding to the alternative $C_6H_5CS^+$ fragment ions.

Electrochemical studies

Cyclic voltammetry was used to determine the half-wave potentials of the osmium(III)–osmium(II) couples. Voltammograms were recorded at potential scan rates over the range 0.010–0.200 V s^{-1} at a platinum electrode for 10^{-3} mol dm^{-3} solutions of the complexes in DMF–NBu^n_4 PF_6 (0.1 mol dm^{-3}). Analysis of the cyclic voltammograms obtained indicated that the electroreduction process can be described as a quasi-reversible process where $i_{p,a}$ is proportional to the square root of the potential sweep rate but the potential difference between $E_{p,a}$ and $E_{p,c}$ is in the range 0.080–0.120 V. the reduction potentials observed and the peak-to-peak separations ($\Delta E = E_{p,a}$-$E_{p,c}$) are reported in Table 2, for a potential sweep rate of 0.050 V s^{-1}. It can be seen that the half-wave potentials are only weakly dependent on the thiolate ligand and they are nearly independent on the substituent group of the monothiocarboxylate ligand. In contrast, compounds bearing a larger number of R′COS ligands show significant variations of their $E_{1/2}$ values[12] with the nature of R′.

Complexes **1** and **2** have been structurally characterized for R′ = Me. The X-ray diffraction of $[Os(SC_6F_5)_2(SOCCH_3)(PMe_2Ph)_2]$ (**1a**) (Fig. 1) shows an octahedral coordination geometry with

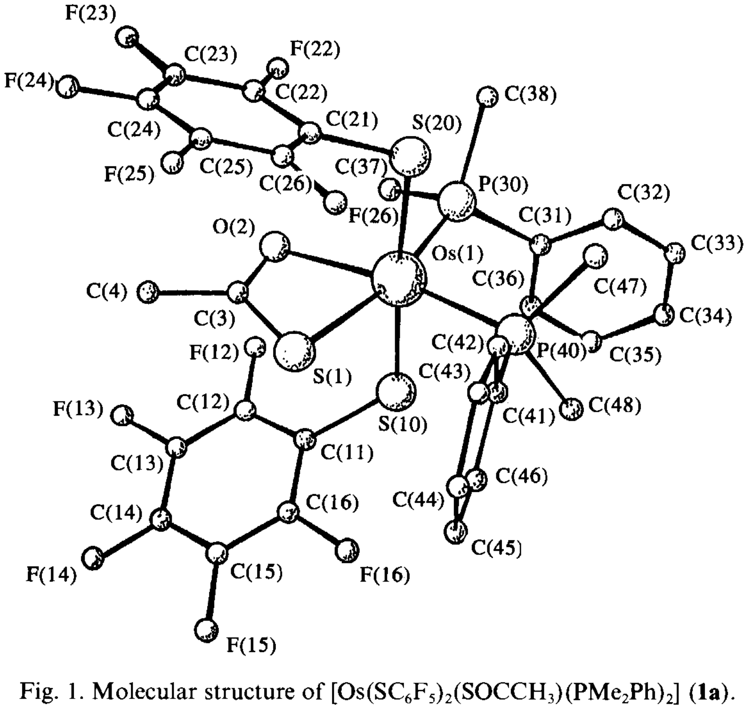

Fig. 1. Molecular structure of $[Os(SC_6F_5)_2(SOCCH_3)(PMe_2Ph)_2]$ (**1a**).

trans-thiolates, *cis*-phosphines and chelating monothioacetate ligand. Molecular dimensions are listed in Table 3. The structure resembles that of the $[Os(SC_6F_5)_2(O_2CPh)(PMe_2Ph)_2]$[7] (**3**) analogue in which the benzoate ligand occupies the place of the monothioacetate ligand. The *trans* Os—S distances in $[Os(SC_6F_5)_2(SOCCH_3)(PMe_2Ph)_2]$ (**1a**) are very similar to the corresponding *trans* Os—S distances in $[Os(SC_6F_5)_2(O_2CPh)(PMe_2Ph)_2]$ (**3**), ie. 2.3313(14) and 2.3466(14) *vs* 2.239(1) and 2.335(1). Both Os—P distances in the carboxylate compound (**3**) are very similar [2.293(1) and 2.300(1)] but for the monothiocarboxylate compound (**1a**) the Os—P distance *trans* to the S atom of the monothiocarboxylate group is longer than the Os—P distance *trans* to the oxygen atom [2.32446(14) and 2.299(2) respectively]. In **1a** the Os—S (monothiocarboxylate) distance is larger than the Os—S(thiolate) distances [2.4447(13) *vs* 2.3389(14) (mean) respectively].

The X-ray crystal structure of $[Os(SC_6F_4H\text{-}4)_2(SOCCH_3)(PMe_2Ph)_2]$ (**2a**) shows the same arrangement and conformation of the ligands as those found for **1a**. The core $[OsS_2(SO)P_2]$ of both **1a** and **2a** shows practically equal bond distances within experimental error, the only significant difference found between **1a** and **2a** relating to the Os—O distances [2.208(4), 2.187(3)]. The molecular dimensions of **2a** are listed in Table 4.

Table 3. Selected bond lengths (Å) and angles (°) for $[Os(SC_6F_5)_2(SOCCH_3)(PMe_2Ph)_2]$, **1a**

(a) Co-ordination sphere of the osmium atom			
Os(1)—S(10)	2.3313(14)	Os(1)—S(20)	2.3466(14)
Os(1)—P(30)	2.3446(14)	Os(1)—P(40)	2.299(2)
Os(1)—S(1)	2.4447(13)	Os(1)—O(2)	2.208(4)
S(10)—Os(1)—S(20)	176.27(5)	P(30)—Os(1)—P(40)	96.50(5)
S(10)—Os(1)—P(30)	87.20(5)	S(20)—Os(1)—P(30)	90.26(5)
S(10)—Os(1)—P(40)	89.96(5)	S(20)—Os(1)—P(40)	87.62(5)
S(10)—Os(1)—O(2)	90.81(10)	S(20)—Os(1)—O(2)	92.20(10)
P(30)—Os(1)—O(2)	96.70(10)	P(40)—Os(1)—O(2)	166.80(10)
S(10)—Os(1)—S(1)	92.08(5)	S(20)—Os(1)—S(1)	91.16(5)
P(30)—Os(1)—S(1)	162.47(5)	P(40)—Os(1)—S(1)	101.02(5)
O(2)—Os(1)—S(1)	65.79(10)		
(b) Pentafluorothiophenolate ligands			
S(10)—C(11)	1.776(5)	S(20)—C(21)	1.757(5)
Os(1)—S(10)—C(11)	109.4(2)	Os(1)—S(20)—C(21)	107.7(2)
(c) Dimethylphenylphosphine ligands			
P(30)—C(31)	1.831(3)	P(40)—C(41)	1.820(3)
P(30)—C(37)	1.832(7)	P(40)—C(47)	1.805(6)
P(30)—C(38)	1.842(6)	P(40)—C(48)	1.816(6)
Os(1)—P(30)—C(31)	119.35(14)	Os(1)—P(40)—C(41)	109.6(2)
Os(1)—P(30)—C(37)	109.1(2)	Os(1)—P(40)—C(47)	119.1(2)
Os(1)—P(30)—C(38)	116.1(2)	Os(1)—P(40)—C(48)	118.6(2)
C(31)—P(30)—C(37)	104.2(3)	C(41)—P(40)—C(47)	102.5(2)
C(31)—P(30)—C(38)	102.9(3)	C(41)—P(40)—C(48)	104.8(3)
C(37)—P(30)—C(38)	103.5(3)	C(47)—P(40)—C(48)	100.2(3)
(d) Thioacetate ligand			
S(1)—C(3)	1.694(6)	O(2)—C(3)	1.275(6)
C(3)—C(4)	1.511(8)		
Os(1)—S(1)—C(3)	79.3(2)	Os(1)—O(2)—C(3)	98.3(3)
S(1)—C(3)—O(2)	116.5(4)	S(1)—C(3)—C(4)	123.7(4)
O(2)—C(3)—C(4)	119.8(5)		

Table 4. Selected bond lengths (Å) and angles (°) for $[Os(SC_6F_4H\text{-}4)_2(SOCCH_3)(PMe_2Ph)_2]$, **2a**

(a) Co-ordination sphere of the osmium atom			
Os(1)—S(10)	2.3458(12)	Os(1)—S(20)	2.3293(12)
Os(1)—P(30)	2.3535(12)	Os(1)—P(40)	2.2975(12)
Os(1)—S(1)	2.4476(12)	Os(1)—O(2)	2.187(3)
S(10)—Os(1)—S(20)	176.52(4)	P(30)—Os(1)—P(40)	96.22(4)
S(10)—Os(1)—P(30)	87.81(4)	S(20)—Os(1)—P)30)	90.65(4)
S(10)—Os(1)—P(40)	89.97(4)	S(20)—Os(1)—P(40)	87.09(4)
S(10)—Os(1)—O(2)	91.32(8)	S(20)—Os(1)—O(2)	91.97(9)
P(30)—Os(1)—O(2)	97.02(9)	P(40)—Os(1)—O(2)	166.73(9)
S(10)—Os(1)—S(1)	91.76(4)	S(20)—Os(1)—S(1)	90.64(4)
P(30)—Os(1)—S(1)	162.67(4)	P(40)—Os(1)—S(1)	101.11(4)
O(2)—Os(1)—S(1)	65.66(9)		
(b) 2,3,5,6-tetrafluorothiophenolate ligands			
S(10)—C(11)	1.765(5)	S(20)—C(21)	1.766(5)
Os(1)—S(10)—C(11)	108.8(2)	Os(1)—S(20)—C(21)	108.9(2)
(c) Dimethylphenylphosphine ligands			
P(30)—C(31)	1.827(3)	P(40)—C(41)	1.812(3)
P(30)—C(37)	1.808(5)	P(40)—C(47)	1.817(5)
P(30)—C(38)	1.816(6)	P(40)—C(48)	1.816(5)
Os(1)—P(30)—C(31)	119.27(12)	Os(1)—P(40)—C(41)	108.91(13)
Os(1)—P(30)—C(37)	109.6(2)	Os(1)—P(40)—C(47)	118.5(2)
Os(1)—P(30)—C(38)	116.8(3)	Os(1)—P(40)—C(48)	118.7(2)
C(31)—P(30)—C(37)	103.9(2)	C(41)—P(40)—C(47)	103.3(2)
C(31)—P(30)—C(38)	102.9(2)	C(41)—P(40)—C(48)	104.8(2)
C(37)—P(30)—C(38)	102.3(3)	C(47)—P(40)—C(48)	100.8(2)
(d) Thioacetate ligand			
S(1)—C(3)	1.698(5)	O(2)—C(3)	1.269(5)
C(3)—C(4)	1.504(7)		
Os(1)—S(1)—C(3)	79.1(2)	Os(1)—O(2)—C(3)	99.5(3)
S(1)—C(3)—O(2)	115.7(3)	S(1)—C(3)—C(4)	124.2(4)
O(2)—C(3)—C(4)	120.0(4)		

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