Complexes of the Platinum Metals. Part 33.[1] Synthesis of Some Ruthenium and Osmium Sulphonate Derivatives: *X*-Ray Crystal Structure of Aqua(carbonyl)-bis(toluene-*p*-sulphonato)bis(triphenylphosphine)ruthenium(II) *

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Sulphonic acids RSO_3H (R = CH_3, CF_3, or $C_6H_4CH_3$-*p*) react with the precursors $[MH_2(CO)(PPh_3)_3]$ (M = Ru or Os) and $[Ru(CO)_3(PPh_3)_2]$ or $[OsH_2(CO)_2(PPh_3)_2]$ in refluxing benzene or toluene to afford the complexes $[M(O_3SR)_2(H_2O)(CO)(PPh_3)_2]$ and $[M(O_3SR)_2(CO)_2(PPh_3)_2]$ respectively. The precursors $[RuH_2(PPh_3)_4]$ and $[OsH_4(PPh_3)_3]$ react with sulphonic acids in refluxing benzene to give the η^6-benzene complexes $[MH(\eta^6\text{-}C_6H_6)(PPh_3)_2][O_3SR]$. However a similar reaction in refluxing ethanol yielded $[OsH_3(PPh_3)_4][O_3SCF_3]$. The complexes $[Ru(O_3SR)_2(H_2O)(CO)(PPh_3)_2]$ have been shown by variable-temperature ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectroscopy to be fluxional in solution. The solid-state structure of one example, $[Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$ has been determined by *X*-ray diffraction methods. The crystals are monoclinic, space group $P2_1/n$, with a = 24.382(5), b = 18.075(4), c = 10.729(2) Å, β = 99.03(2)°, and Z = 4. The octahedral ruthenium(II) complex contains monodentate sulphonate ligands (*trans* to PPh_3 and CO) and an aqua ligand (*trans* to PPh_3) with strong hydrogen-bonding interactions between the H atoms of the H_2O and the non-co-ordinated oxygen atoms of the sulphonate ligands. The molecular structure is very similar to that previously reported for the alcohol dehydrogenation catalyst $[Ru(O_2CCF_3)_2(CH_3OH)(CO)(PPh_3)_2]$.

The present paper, which complements an earlier one on sulphonate complexes of iridium,[1] describes the synthesis and characterisation of some new sulphonate complexes of ruthenium and osmium including sulphonate analogues of the alcohol dehydrogenation catalyst $[Ru(O_2CCF_3)_2(CH_3OH)(CO)(PPh_3)_2]$ previously reported from this laboratory.[2,3] Since the co-ordinating properties of sulphonate anions and the chemistry of their known platinum group metal derivatives were surveyed in the previous paper[1] these topics are not reviewed here. However, mention should be made of a more recent paper by Bailey and Ludi[4] in which new toluene-*p*-sulphonate complexes of ruthenium, relevant to the present work, including $[Ru(O_3SC_6H_4CH_3\text{-}p)(dppe)_2][O_3SC_6H_4CH_3\text{-}p]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), $[Ru(O_3SC_6H_4CH_3\text{-}p)_2(\eta^6\text{-}C_6H_6)(PPh_3)]$, and $[Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)_2L_2]$ (L = PPh_3 or tetrahydrofuran) are reported.

A preliminary account of the present results was given in our earlier publication on sulphonate complexes of the platinum group metals.[5]

Experimental

Ruthenium and osmium salts were supplied by Johnson Matthey plc and were converted into the phosphine complexes carbonyldihydridotris(triphenylphosphine)-ruthenium and -osmium, tricarbonylbis(triphenylphosphine)ruthenium, dicarbonyldihydridobis(triphenylphosphine)osmium,[6] dihydridotetrakis(triphenylphosphine)ruthenium,[7] and tetrahydridotris(triphenylphosphine)osmium[6] by standard literature procedures. Other experimental details are similar to those reported in ref. 1. Spectroscopic data are given in Tables 1 and 2.

Ruthenium Sulphonate Complexes.—Aqua(carbonyl)bis(methanesulphonato)bis(triphenylphosphine)ruthenium(II). Methanesulphonic acid (0.04 cm^3, 0.654 mmol) was added to a stirred solution of carbonyldihydridotris(triphenylphosphine)ruthenium (0.2 g, 0.218 mmol) in benzene (10 cm^3). The mixture was heated under reflux for 2 h to give a yellow solution then cooled, filtered, and evaporated under reduced pressure to form a yellow solid which was twice crystallised from dichloromethane–diethyl ether. Filtration followed by washing with ethanol and n-hexane gave large yellow crystals. Yield 0.17 g, 80%; m.p. 176—184 °C (Found: C, 54.35; H, 4.40. $C_{39}H_{38}O_8P_2RuS_2$ requires C, 54.35; H, 4.45%). Aqua(carbonyl)bis(trifluoromethanesulphonato)bis(triphenylphosphine)ruthenium(II) was similarly prepared and, after two crystallisations from dichloromethane–n-hexane, was isolated as yellow *crystals*. Yield 95%, m.p. 187—190 °C (Found: C, 48.65; H, 3.45. $C_{39}H_{32}F_6O_8P_2RuS_2$ requires C, 48.30; H, 3.35%). Aqua(carbonyl)bis(toluene-*p*-sulphonato)bis(triphenylphosphine)ruthenium(II) was similarly prepared and, after crystallisation from dichloromethane–diethyl ether, yielded well formed yellow *crystals*. Yield 86%, m.p. 176—184 °C (Found: C, 60.1; H, 4.65. $C_{51}H_{46}O_8P_2RuS_2$ requires C, 60.40; H, 4.55%).

Dicarbonylbis(methanesulphonato)bis(triphenylphosphine)ruthenium(II). Methanesulphonic acid (0.08 cm^3, 1.23 mmol) was added to a stirred suspension of tricarbonylbis(triphenylphosphine)ruthenium (0.23 g, 0.34 mmol) in benzene (10 cm^3) and the mixture heated under reflux for 1 h. The yellow solution was cooled, filtered, diluted with methanol (25 cm^3), and then concentrated under reduced pressure whereupon a white microcrystalline solid deposited. This was filtered off, washed with diethyl ether and light petroleum (b.p. 60—80 °C), then recrystallised from dichloromethane–n-hexane to afford white microcrystals. Yield 0.14 g, 50%; m.p. 200—203 °C (Found: C, 55.0; H, 4.15. $C_{40}H_{36}O_8P_2RuS_2$ requires C, 55.10; H, 4.15%).

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Dicarbonylbis(trifluoromethanesulphonato)bis(triphenylphosphine)ruthenium(II) was similarly prepared and isolated as white *crystals*. Yield 55%, m.p. 255—258 °C (Found: C, 50.05; H, 3.25. $C_{40}H_{30}F_6O_8P_2RuS_2$ requires C, 49.05; H, 3.10%).

Dicarbonylbis(*toluene*-p-*sulphonato*)*bis*(*triphenylphosphine*)-*ruthenium*(II). A solution of toluene-*p*-sulphonic acid (0.22 g, 1.16 mmol) in ethanol (2 cm^3) was added to a stirred suspension of tricarbonylbis(triphenylphosphine)ruthenium (0.4 g, 0.56 mmol) in benzene (10 cm^3) and the mixture heated under reflux for 1 h. The yellow solution was cooled, filtered, diluted with methanol (*ca.* 35 cm^3), and concentrated under reduced pressure whereupon a white solid deposited. This was filtered off, washed with diethyl ether and light petroleum (b.p. 60—80 °C), then crystallised from dichloromethane–n-hexane and dried *in vacuo* to give white microcrystals. Yield 0.33 g, 57%; m.p. 251—253 °C (Found: C, 60.6; H, 4.25. $C_{52}H_{44}O_8P_2RuS_2$ requires C, 61.0; H, 4.35%).

(η^6-*Benzene*)*hydridobis*(*triphenylphosphine*)*ruthenium*(II) *methanesulphonate–dichloromethane* (1/1). Dihydridotetrakis(triphenylphosphine)ruthenium (0.4 g, 0.347 mmol) was added to stirred, nitrogen-purged benzene (20 cm^3) and after *ca.* 5 min methanesulphonic acid (0.05 cm^3, 0.76 mmol) was added and the resulting red-brown mixture was heated under reflux for 1 h to give a yellow-brown solution. After cooling, the solution was filtered and then evaporated under reduced pressure to give a yellow-brown oil which was crystallised from dichloromethane–diethyl ether and washed with diethyl ether and light petroleum. Recrystallisation from dichloromethane–diethyl ether gave yellow needle crystals. Yield 0.205 g, 68%; m.p. 185—190 °C (Found: C, 59.5; H, 4.80. $C_{44}H_{42}Cl_2O_3P_2RuS$ requires C, 59.7; H, 4.80%). (η^6-Benzene)hydridobis(triphenylphosphine)ruthenium(II) trifluoromethanesulphonate–dichloromethane (1/1) was similarly prepared and crystallised as yellow needle-like crystals. Yield 43%, m.p. 199—202 °C (Found: C, 56.35; H, 4.20. $C_{44}H_{39}Cl_2F_3O_3P_2RuS$ requires C, 56.3; H, 4.20%).

Osmium Sulphonato Complexes.—*Aqua*(*carbonyl*)*bis*(*methanesulphonato*)*bis*(*triphenylphosphine*)*osmium*(II). Methanesulphonic acid (0.05 cm^3, 0.745 mmol) was added to a stirred solution of carbonyldihydridotris(triphenylphosphine)osmium (0.25 g, 0.248 mmol) in benzene (10 cm^3). The mixture was heated under reflux for 2 h to give a yellow solution which was then cooled, filtered and evaporated to dryness. The residue was crystallised from dichloromethane–n-hexane then washed with ethanol and recrystallised from dichloromethane–n-hexane as yellow prisms. Yield 0.2 g, 83%; m.p. 270—273 °C (Found: C, 48.75; H, 3.95. $C_{39}H_{38}O_8OsP_2S_2$ requires C, 49.25; H, 4.05%).

Aqua(*carbonyl*)*bis*(*toluene*-p-*sulphonato*)*bis*(*triphenylphosphine*)*osmium*(II). A solution of toluene-*p*-sulphonic acid monohydrate (0.28 g, 1.49 mmol) in ethanol (2 cm^3) was added to a stirred solution of carbonyldihydridotris(triphenylphosphine)osmium (0.25 g, 0.248 mmol) in benzene (10 cm^3). The mixture was heated under reflux for 2 h to form a yellow solution which was worked up as described above to give pale yellow needle-like crystals. Yield 0.13 g, 48%; m.p. 210—221 °C (Found: C, 55.55; H, 4.35. $C_{51}H_{46}O_8OsP_2S_2$ requires C, 55.5; H, 4.20%).

Dicarbonylbis(*methanesulphonato*)*bis*(*triphenylphosphine*)-*osmium*(II). Methanesulphonic acid (0.016 cm^3, 0.249 mmol) was added to a stirred suspension of dicarbonyldihydridobis(triphenylphosphine)osmium (0.4 g, 0.518 mmol) in toluene (20 cm^3). The mixture was heated under reflux for 4 h to give a yellow solution. On cooling this was filtered and then evaporated under reduced pressure to give white crystals in a brown oily residue. These were twice crystallised from dichloromethane–diethyl ether to give white crystals. Yield 0.23 g, 46%; m.p. 310—312 °C (Found: C, 49.8; H, 3.70. $C_{40}H_{36}O_8OsP_2S_2$ requires C, 50.0; H, 3.80%). Dicarbonylbis(trifluoromethanesulphonato)bis(triphenylphosphine)osmium(II) was similarly prepared and twice crystallised from dichloromethane–diethyl ether to give white crystals. Yield 53%, m.p. 303—304 °C (Found: C, 45.1; H, 2.85. $C_{40}H_{30}F_6O_8OsP_2S_2$ requires C, 44.95; H, 2.85%).

Dicarbonylbis(*toluene*-p-*sulphonato*)*bis*(*triphenylphosphine*)-*osmium*(II). A solution of toluene-*p*-sulphonic acid monohydrate (0.32 g, 1.66 mmol) in ethanol (2 cm^3) was added to a stirred suspension of dicarbonyldihydridobis(triphenylphosphine)osmium (0.32 g, 0.414 mmol) in toluene (20 cm^3). The mixture was heated under reflux for 8 h to give a pale yellow solution which was worked up as described above to give white microcrystals. Yield 0.2 g, 35%; m.p. 262—265 °C (Found: C, 55.7; H, 4.00. $C_{52}H_{44}O_8OsP_2S_2$ requires C, 56.10; H, 4.0%).

(η^6-*Benzene*)*hydridobis*(*triphenylphosphine*)*osmium*(II) *trifluoromethanesulphonate–dichloromethane* (1/1). Trifluoromethanesulphonic acid (0.08 cm^3, 0.917 mmol) was added to a suspension of tetrahydridotris(triphenylphosphine)osmium (0.3 g, 0.306 mmol) in benzene (20 cm^3). The mixture was heated under reflux for 1 h to give a yellow-brown solution. This was cooled, filtered, and then evaporated under reduced pressure to leave a yellow-brown oil. Crystallisation of the oil from dichloromethane–n-hexane followed by washing with ethanol and light petroleum and a further crystallisation from dichloromethane–n-hexane gave yellow crystals. Yield 0.11 g, 35%; m.p. 220—223 °C (Found: C, 51.95; H, 3.85. $C_{44}H_{39}Cl_2F_3O_3OsP_2S$ requires C, 51.4; H, 3.80%). (η^6-Benzene)hydridobis(triphenylphosphine)osmium(II) methanesulphonate–dichloromethane (1/1) was similarly prepared and isolated as yellow crystals. Yield 17%, m.p. 183—190 °C (Found: C, 53.40; H, 4.45. $C_{44}H_{42}Cl_2O_3OsP_2S$ requires C, 54.3; H, 4.35%).

Trihydridotetrakis(*triphenylphosphine*)*osmium*(IV) *trifluoromethanesulphonate*. Trifluoromethanesulphonic acid (0.12 cm^3, 1.36 mmol) was added to a suspension of tetrahydridotris(triphenylphosphine)osmium (0.46 g, 0.469 mmol) in ethanol (20 cm^3) and the mixture was heated under reflux for 1 h to give a yellow-brown solution. After cooling the solution was filtered and concentrated under reduced pressure to give glittering white crystals. These were filtered off, washed with ethanol and diethyl ether, then dried *in vacuo*. Yield 0.05 g, 7.5%; m.p. 217—229 °C (Found: C, 62.40; H, 4.75. $C_{73}H_{63}F_3O_3OsP_4S$ requires C, 63.00; H, 4.55%). Addition of free triphenylphosphine (1 mmol) to the reaction mixture increased the yield to 0.47 g (72%).

X-*Ray Structural Analysis of* $[Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$.—*Crystal data.* Crystals were obtained from dichloromethane–diethyl ether in the presence of traces of water. $C_{51}H_{46}O_8P_2RuS_2$, $M = 1\,014.06$, monoclinic, $a = 24.382(5)$, $b = 18.075(4)$, $c = 10.729(2)$ Å, $\beta = 99.03(2)°$, $U = 4\,652.76$ Å^3, space group $P2_1/n$ (alternative $P2_1/c$), $Z = 4$, $D_c = 1.592$ g cm^{-3}, $F(000) = 2\,088$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 4.78$ cm^{-1}.

Data collection and processing. The *X*-ray analysis was performed using 5 114 reflections with $I/\sigma(I) \geqslant 3.0$ measured in the θ range 3—25° on a Phillips PW1100 four-circle diffractometer using Mo-K_α radiation from a graphite-crystal monochromator. The methods of data collection and processing have been described previously.[8]

Structure analysis and refinement.[9] Full-matrix least-squares procedures were used in the refinement of positional and thermal parameters for all non-hydrogen atoms. The ruthenium, phosphorus, sulphur, oxygen, and non-phenyl carbon atoms were assigned anisotropic thermal parameters. Hydrogen atoms, which were given fixed thermal parameters ($U = 0.08$ Å^2), were allowed to 'ride' on the carbon atoms in the rings (C–H 1.08 Å). The hydrogen atoms of the co-ordinated water molecule were located from a difference Fourier synthesis

Table 1. Infrared and n.m.r. spectroscopic data

Complex	$\tilde{\nu}$(MH)/cm^{-1}	$\tilde{\nu}$(CO)/cm^{-1}	δ(MH)/p.p.m.	*J*(PH)/Hz	δ(P)/p.p.m.	Others
$[Ru(O_3SCH_3)_2(H_2O)(CO)(PPh_3)_2]$		1 990			*	
$[Ru(O_3SCF_3)_2(H_2O)(CO)(PPh_3)_2]$		1 989			*	
$[Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$		1 988			*	
$[Ru(O_3SCH_3)_2(CO)_2(PPh_3)_2]$		2 059, 1 987			22.73 (s)	
$[Ru(O_3SCF_3)_2(CO)_2(PPh_3)_2]$		2 080, 2 021			22.76 (s)	δ(F) − 78.56 (s)
$[Ru(O_3SC_6H_4CH_3\text{-}p)_2(CO)_2(PPh_3)_2]$		2 065, 2 003			21.03 (s)	
$[RuH(\eta^6\text{-}C_6H_6)(PPh_3)_2][O_3SCH_3]$	2 036		−9.21 (t)	*ca.* 37	51.03 (s)	
$[RuH(\eta^6\text{-}C_6H_6)(PPh_3)_2][O_3SCF_3]$	2 041		−9.16 (t)	*ca.* 37	50.87 (s)	δ(F) − 78.36 (s)
$[Os(O_3SCH_3)_2(H_2O)(CO)(PPh_3)_2]$		1 953			*	
$[Os(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$		1 970			*	
$[Os(O_3SCH_3)_2(CO)_2(PPh_3)_2]$		2 045, 1 966			2.06 (s)	
$[Os(O_3SCF_3)_2(CO)_2(PPh_3)_2]$		2 062, 1 992			0.69 (s)	δ(F) − 76.97 (s)
$[Os(O_3SC_6H_4CH_3\text{-}p)_2(CO)_2(PPh_3)_2]$		2 053, 1 973			1.13 (s)	
$[OsH(\eta^6\text{-}C_6H_6)(PPh_3)_2][O_3SCH_3]$	2 127		−11.27 (t)	*ca.* 34	6.22	
$[OsH(\eta^6\text{-}C_6H_6)(PPh_3)_2][O_3SCF_3]$	2 130		−11.21 (t)	*ca.* 34	6.18	δ(F) − 78.37 (s)
$[OsH(\eta^6\text{-}C_6H_6)(PPh_3)_2][O_3SC_6H_4CH_3\text{-}p]$	2 138		−11.32 (t)	*ca.* 31	6.30 (s)	
$[OsH_3(PPh_3)_4][O_3SCF_3]$	2 126		−9.86 (q)	*ca.* 19.6	2.14 (s)	

* See Table 2.

Table 2. Variable-temperature n.m.r. data

Complex	*T*/K	δ(P)/p.p.m.	*J*(PP′)/Hz	δ(CH$_3$)/p.p.m.
$[Ru(O_3SCH_3)_2(H_2O)(CO)(PPh_3)_2]$	323	41.86 (s)		2.44 (s), 2.30 (s)
	223	$\left.\begin{matrix}43.23\\39.73\end{matrix}\right\}$AB 42.07 (s)	32	
$[Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$	323	41.26 (s)		2.36 (s), 2.25 (s)
	223	$\left.\begin{matrix}43.94\\39.50\end{matrix}\right\}$AB 42.03 (s)	31	2.44 (s), 2.40 (s), 2.38 (s), 2.28 (s)
$[Os(O_3SCH_3)_2(H_2O)(CO)(PPh_3)_2]$	323	Incomplete coalescence		2.42 (s), 2.29 (s)
	223	$\left.\begin{matrix}-6.84\\-5.43\end{matrix}\right\}$AB −4.76 (s)	13	
$[Os(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$	323	Incomplete coalescence		2.37 (s), 2.27 (s)
	223	$\left.\begin{matrix}-7.12\\-3.79\end{matrix}\right\}$AB −5.24 (s)	13	

calculated using data with $(\sin\theta)/\lambda < 0.35$. These were included in structure-factor calculations ($U = 0.8$ Å^2) but were not refined. A final R value of 0.0681 and R' of 0.0687 [weighting scheme, $w = 1/\sigma^2(I)$] were obtained with 397 independent parameters. Positional parameters for non-hydrogen atoms are given in Table 3, selected bond length and angle data in Table 4.

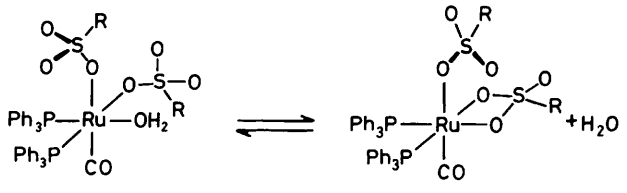
Results and Discussion

Our interest in sulphonate complexes centres on the potential of the sulphonate anion as a leaving group in platinum metal ligand-substitution reactions. In this paper we describe the synthesis and characterisation of new sulphonate complexes; some of the chemistry of these systems will be reported in a later paper.

$[M(O_3SR)_2(H_2O)(CO)(PPh_3)_2]$ (M = Ru *or* Os).—These air-stable yellow crystalline complexes are prepared by treatment of the precursors $[MH_2(CO)(PPh_3)_3]$ with sulphonic acids in boiling benzene; the aqua ligands are believed to arise from residual traces of water associated with the sulphonic acids or the solvent employed. The stoicheiometry, in particular the presence of the H_2O ligand, and the stereochemistry of these complexes in the solid state have been conclusively established by the *X*-ray diffraction study on the ruthenium toluene-*p*-sulphonate derivative (see below) which revealed the structure (**A**) shown in the Scheme. However, the ^1H, ^{19}F, and ^{31}P-$\{^1H\}$ n.m.r. spectra show temperature-dependent behaviour indicative of the occurrence of fluxional processes in solution. The relevant n.m.r. data, which are summarised in Table 2, are consistent with a process (Scheme) which equilibrates the PPh_3 ligands but not the O_3SR groups ($R = CH_3$ or $C_6H_4CH_3\text{-}p$) at elevated temperatures and which gives rise to two species, one containing equivalent PPh_3 ligands, and one containing non-equivalent PPh_3 ligands on cooling to ambient temperature or below. For example the ^{31}P-$\{^1H\}$ and ^1H n.m.r. spectra of the ruthenium complex $[Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$ taken at elevated temperature (323 K) show a singlet attributable to equivalent ^{31}P nuclei and two singlets arising

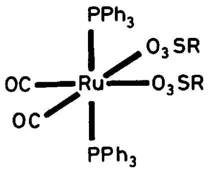
Table 3. Fractional atomic co-ordinates for [Ru($O_3SC_6H_4CH_3$-*p*)$_2$(H_2O)(CO)(PPh_3)$_2$]. Estimated standard deviations (e.s.d.s) are given in parentheses

Atom	*x*	*y*	*z*
Ru	0.132 31(3)	0.228 11(3)	−0.176 82(6)
P(1)	0.060 70(9)	0.312 55(11)	−0.245 80(22)
P(2)	0.130 19(9)	0.142 41(11)	−0.345 09(21)
S(1)	0.254 3(1)	0.190 6(1)	−0.025 0(2)
O(11)	0.199 9(2)	0.160 6(3)	−0.083 0(5)
O(12)	0.247 0(3)	0.244 5(3)	0.073 0(7)
O(13)	0.286 6(3)	0.215 6(4)	−0.118 1(7)
S(2)	0.064 1(1)	0.145 5(1)	0.045 2(2)
O(21)	0.080 3(2)	0.156 9(3)	−0.082 7(5)
O(22)	0.079 4(3)	0.210 9(3)	0.125 3(6)
O(23)	0.007 7(3)	0.121 7(4)	0.036 8(6)
O(3w)	0.142 6(2)	0.292 7(3)	−0.000 2(5)
C	0.175 6(3)	0.286 2(4)	−0.258 9(8)
O	0.201 6(3)	0.324 6(3)	−0.314 5(6)
C(311)	0.289 7(4)	0.113 6(5)	0.053 2(9)
C(312)	0.325 8(4)	0.125 2(6)	0.163 9(10)
C(313)	0.356 2(5)	0.066 8(7)	0.222 1(11)
C(314)	0.350 2(5)	−0.003 8(7)	0.171 0(13)
C(315)	0.312 5(5)	−0.014 6(6)	0.058 8(11)
C(316)	0.281 3(4)	0.044 4(5)	−0.000 0(10)
C(317)	0.386 4(6)	−0.069 4(7)	0.234 0(15)
C(411)	0.106 0(4)	0.072 6(5)	0.116 7(8)
C(412)	0.084 3(5)	0.000 7(5)	0.118 6(9)
C(413)	0.117 7(6)	−0.053 4(6)	0.177 3(11)
C(414)	0.171 6(6)	−0.041 3(7)	0.234 0(10)
C(415)	0.193 9(5)	0.031 6(6)	0.233 9(10)
C(416)	0.160 0(4)	0.086 8(5)	0.173 9(9)
C(417)	0.211 0(7)	−0.103 7(8)	0.300 1(13)
C(111)	0.015 9(3)	0.300 7(4)	−0.397 8(8)
C(112)	−0.041 1(4)	0.297 3(5)	−0.412 7(9)
C(113)	−0.072 3(4)	0.282 5(5)	−0.531 1(9)
C(114)	−0.045 0(4)	0.272 1(6)	−0.632 5(10)
C(115)	0.011 2(4)	0.279 6(6)	−0.623 7(10)
C(116)	0.042 2(4)	0.295 0(5)	−0.503 3(9)
C(121)	0.086 3(3)	0.407 8(5)	−0.257 3(8)
C(122)	0.060 3(4)	0.455 7(6)	−0.348 4(10)
C(123)	0.080 0(4)	0.528 7(6)	−0.357 7(11)
C(124)	0.125 6(4)	0.552 6(6)	−0.278 9(10)
C(125)	0.153 5(4)	0.507 2(6)	−0.184 1(10)
C(126)	0.131 6(4)	0.434 6(5)	−0.174 7(10)
C(131)	0.012 8(3)	0.322 6(5)	−0.132 1(8)
C(132)	0.012 3(4)	0.386 7(5)	−0.057 7(9)
C(133)	−0.023 9(4)	0.392 9(6)	0.026 4(10)
C(134)	−0.062 3(4)	0.337 5(6)	0.040 1(10)
C(135)	−0.062 7(4)	0.274 3(6)	−0.032 9(10)
C(136)	−0.024 3(3)	0.266 7(5)	−0.117 5(8)
C(211)	0.154 6(3)	0.048 3(4)	−0.294 3(8)
C(212)	0.141 1(4)	0.018 5(5)	−0.185 5(9)
C(213)	0.153 9(4)	−0.055 7(6)	−0.154 7(10)
C(214)	0.179 3(4)	−0.098 7(6)	−0.233 6(9)
C(215)	0.193 2(4)	−0.070 8(6)	−0.342 3(10)
C(216)	0.181 1(4)	0.004 8(5)	−0.374 0(9)
C(221)	0.063 5(3)	0.120 0(4)	−0.440 9(7)
C(222)	0.017 5(3)	0.121 3(4)	−0.384 4(8)
C(223)	−0.034 1(4)	0.100 4(5)	−0.452 3(9)
C(224)	−0.036 7(4)	0.079 1(5)	−0.578 0(9)
C(225)	0.008 7(4)	0.077 0(5)	−0.633 0(9)
C(226)	0.060 9(4)	0.096 1(5)	−0.567 4(8)
C(231)	0.179 5(3)	0.170 5(4)	−0.447 8(8)
C(232)	0.165 1(4)	0.207 0(5)	−0.562 5(8)
C(233)	0.205 2(4)	0.235 4(6)	−0.626 1(10)
C(234)	0.260 7(5)	0.228 4(6)	−0.578 1(11)
C(235)	0.276 4(5)	0.192 5(6)	−0.461 4(11)
C(236)	0.235 1(4)	0.163 5(5)	−0.399 4(9)

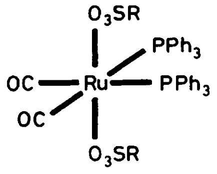


(A) **(B)**

Scheme.



(1a)



(1b)

from the protons of two non-equivalent methyl groups, thereby supporting the occurrence of the rapid fluxional reaction shown in the Scheme which equilibrates the PPh_3 ligands but *not* the CH_3 groups. At lower temperatures the process is frozen out to give a static mixture of (**A**) and (**B**) which generates four non-equivalent CH_3 signals [two from (**A**), two from (**B**)], a ^{31}P-{^1H} AB pattern [from (**A**)], and a ^{31}P-{^1H} singlet [from (**B**)]. The somewhat less labile osmium analogues [Os(O_3SR)$_2$(H_2O)(CO)(PPh_3)$_2$] show similar low-temperature n.m.r. patterns but these do not fully coalesce at our high-temperature limit (323 K). These results imply that the M–O_3SR bonds *trans* to CO are less labile than those *trans* to PPh_3. This conclusion is supported by our earlier results[10] on the related [Ru(O_2CR)$_2$(CH_3OH)(CO)(PPh_3)$_2$] system which revealed that the Ru–O_2CR linkages *trans* to CO were less labile than those *trans* to PPh_3. Finally we note that similar fluxional behaviour involving interchange of monodentate, bidentate, and anionic toluene-*p*-sulphonate groups has recently been reported[4] for the ruthenium complex [Ru($O_3SC_6H_4CH_3$-*p*)(dppe)$_2$][$O_3SC_6H_4CH_3$-*p*].

[M(O_3SR)$_2$(CO)$_2$(PPh_3)$_2$].—These air-stable white crystalline complexes are prepared by treating [Ru(CO)$_3$(PPh_3)$_2$] and [OsH_2(CO)$_2$(PPh_3)$_2$] with sulphonic acids in refluxing benzene and toluene respectively. Their spectroscopic data (Table 1) are consistent with the presence of a pair of *cis* carbonyl ligands and two equivalent PPh_3 ligands and thus establish the stereochemistry as (**1a**) or (**1b**). The sterically preferred *trans*-PPh_3 structure (**1a**) is also indicated by the ^{13}C-{^1H} n.m.r. spectra of the co-ordinated PPh_3 ligands which display 'triplet' splitting patterns indicative of virtual coupling to two ^{31}P nuclei for all aromatic carbon atoms save those in the *para* positions.

[MH(η^6-C_6H_6)(PPh_3)$_2$][O_3SR].—These complexes are obtained as yellow air-stable crystalline solids by treatment of [RuH_2(PPh_3)$_4$] and [OsH_4(PPh_3)$_3$] with sulphonic acids RSO_3H (R = CH_3 or CF_3) in boiling benzene. They are characterised by spectroscopic data (Table 1) which are in good

Table 4. Selected bond lengths (Å) and angles (°) for $[Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$

Ru–P(1)	2.347(2)	Ru–P(2)	2.370(2)	S(1)–O(11)	1.476(5)	S(1)–O(12)	1.464(7)
Ru–O(11)	2.165(5)	Ru–O(21)	2.162(6)	S(1)–O(13)	1.435(8)	S(1)–C(311)	1.775(9)
Ru–O(3w)	2.202(6)	Ru–C	1.810(9)	S(2)–O(21)	1.498(6)	S(2)–O(22)	1.472(6)
P(1)–C(111)	1.825(8)	P(1)–C(121)	1.841(9)	S(2)–O(23)	1.428(7)	S(2)–C(411)	1.766(9)
P(1)–C(131)	1.822(9)	P(2)–C(211)	1.853(8)	C–O	1.165(11)		
P(2)–C(221)	1.826(8)	P(2)–C(231)	1.823(9)				
P(2)–Ru–P(1)	105.0(1)	O(11)–Ru–P(1)	170.2(2)	C(311)–S(1)–O(11)	104.3(4)	C(311)–S(1)–O(12)	106.7(4)
O(11)–Ru–P(2)	84.8(2)	O(21)–Ru–P(1)	94.2(1)	C(311)–S(1)–O(13)	107.3(4)	S(1)–O(11)–Ru	123.8(3)
O(21)–Ru–P(2)	91.2(2)	O(21)–Ru–O(11)	84.7(2)	O(22)–S(2)–O(21)	110.1(3)	O(23)–S(2)–O(21)	111.8(4)
O(3w)–Ru–P(1)	84.5(2)	O(3w)–Ru–P(2)	170.0(1)	O(23)–S(2)–O(22)	115.5(4)	C(411)–S(2)–O(21)	106.4(4)
O(3w)–Ru–O(11)	85.6(2)	O(3w)–Ru–O(21)	84.9(2)	C(411)–S(2)–O(22)	105.6(4)	C(411)–S(2)–O(23)	106.7(4)
C–Ru–P(1)	86.0(3)	C–Ru–P(2)	87.4(3)	S(2)–O(21)–Ru	139.9(3)	O–C–Ru	177.5(7)
C–Ru–O(11)	95.4(3)	C–Ru–O(21)	178.6(3)	C(112)–C(111)–P(1)	124.2(7)	C(116)–C(111)–P(1)	116.5(6)
C–Ru–O(3w)	96.5(3)	C(111)–P(1)–Ru	121.0(3)	C(122)–C(121)–P(1)	120.7(6)	C(126)–C(121)–P(1)	121.8(7)
C(121)–P(1)–Ru	112.7(3)	C(121)–P(1)–C(111)	102.2(4)	C(132)–C(131)–P(1)	121.7(7)	C(136)–C(131)–P(1)	120.1(7)
C(131)–P(1)–Ru	112.1(3)	C(131)–P(1)–C(111)	104.5(4)	C(212)–C(211)–P(2)	120.1(7)	C(216)–C(211)–P(2)	119.8(7)
C(131)–P(1)–C(121)	102.1(4)	C(211)–P(2)–Ru	114.1(3)	C(222)–C(221)–P(2)	118.0(6)	C(226)–C(221)–P(2)	120.5(6)
C(221)–P(2)–Ru	118.9(3)	C(221)–P(2)–C(211)	100.3(3)	C(232)–C(231)–P(2)	124.5(6)	C(236)–C(231)–P(2)	116.7(7)
C(231)–P(2)–Ru	109.8(3)	C(231)–P(2)–C(211)	102.8(4)	C(312)–C(311)–S(1)	118.9(7)	C(316)–C(311)–S(1)	119.2(7)
C(231)–P(2)–C(221)	109.6(4)	O(12)–S(1)–O(11)	110.1(4)	C(412)–C(411)–S(2)	120.2(7)	C(416)–C(411)–S(2)	119.8(7)
O(13)–S(1)–O(11)	112.1(4)	O(13)–S(1)–O(12)	115.5(4)				

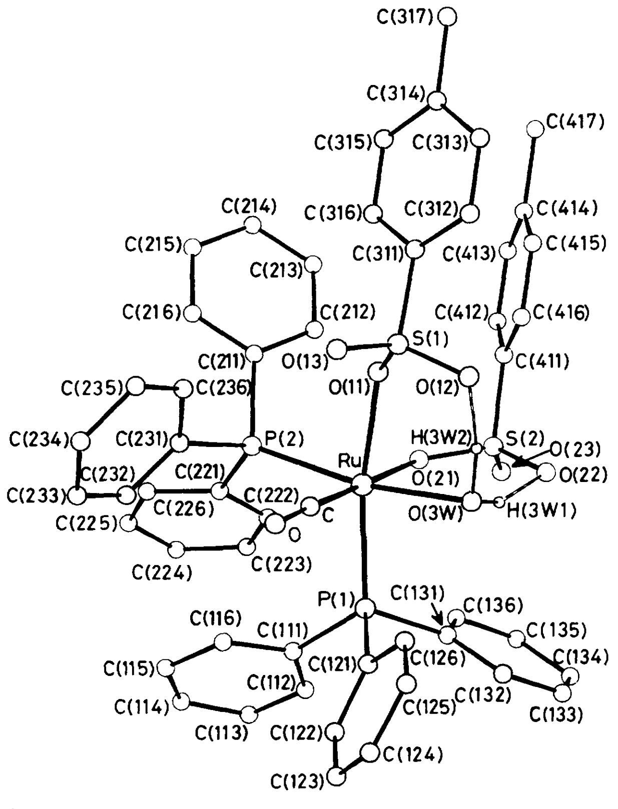


Figure. The molecular structure of $[Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$

agreement with data previously reported for related salts containing the $[MH(\eta^6\text{-}C_6H_6)(PPh_3)_2]^+$ cations.[11,12]

$[OsH_3(PPh_3)_4][O_3SCF_3]$.—Salts containing cations of the form $[OsH_3(PR_3)_4]^+$ were first reported in 1973,[13] and the first example containing the $[OsH_3(PPh_3)_4]^+$ cation was described by Siedle *et al.*[14] while our work was in progress. Our i.r. and ambient-temperature n.m.r. data for $[OsH_3(PPh_3)_4][O_3SCF_3]$ are in good agreement with those reported[14] for $[OsH_3(PPh_3)_4][HC(SO_2CF_3)_2]$ and are characteristic of a fluxional structure in which all three hydride ligands are equivalent and couple equally to all four ^{31}P nuclei. However, Siedle *et al.*[14] have shown that at low temperatures a rigid structure is adopted and have found a trigonally distorted tetrahedral geometry for the OsP_4 skeleton by *X*-ray diffraction methods.

X-Ray Crystal Structure of $[Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$.—The molecular structure of the complex is shown in the Figure, salient bond lengths and bond angles are given in Table 4. The co-ordination geometry about the ruthenium atom, which is essentially octahedral with two monodentate sulphonates, a co-ordinated water molecule, a carbonyl group, and a pair of triphenylphosphine ligands, closely parallels that previously found[3] for the related carboxylate complex $[Ru(O_2CCF_3)_2(CH_3OH)(CO)(PPh_3)_2]$. In each case the complex adopts a sterically unfavourable *cis* arrangement for the bulky triphenylphosphine ligands and displays intramolecular hydrogen-bonding interactions between the non-co-ordinated oxygen atoms of the anionic ligands and the hydroxyl groups of water or methanol. The most noticeable differences between the two structures are found in the Ru–P and Ru–O bond distances, all bar one of which [Ru–P(1)] are slightly longer (*ca.* 0.02—0.06 Å) for the sulphonate complex than for the carboxylate, and in the P–Ru–P bond angle which increases from 99.5° in the carboxylate to 105.0(1)° in the sulphonate. The Ru–OH_2 bond distance [2.202(6) Å] is slightly greater than those found in the complex cations $[RuH(H_2O)(CO)_2(PPh_3)_2]^+$ (2.15 Å)[15] and $[Ru(H_2O)_6]^{2+}$ [2.122(16) Å].[16] The hydrogen-bonded [O–(H) • • • O] distances (2.68 and 2.65 Å) are slightly shorter than those recorded for several intermolecular hydrogen-bonding interactions involving co-ordinated sulphonate and aqua ligands.[15] The distorted tetrahedral geometry about the sulphur atoms is similar to that found in other sulphonate complexes:[17–19] the O–S–O bond angles (mean 112.5°) are greater and the O–S–C bond angles (mean 106.15) are smaller than the tetrahedral angle (109.5°). Finally the S–O bond distances show the expected increase as the external bonding interactions of the oxygen atoms involved strengthen; values are 1.435(8), 1.428(7) (terminal S=O), 1.464(7), 1.472(6) (hydrogen-bonded S=O), and 1.476(5), 1.498(6) Å (ruthenium-bonded S–O).

Acknowledgements

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References

1 Part 32, P. A. Harding and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1987, 947.
2 A. Dobson and S. D. Robinson, *Inorg. Chem.*, 1977, **16**, 137.
3 A. Dobson, D. S. Moore, S. D. Robinson, M. B. Hursthouse, and L. New, *Polyhedron*, 1985, **4**, 1119.
4 O. H. Bailey and A. Ludi, *Inorg. Chem.*, 1985, **24**, 2582.
5 P. A. Harding, M. Preece, S. D. Robinson, and K. Henrick, *Inorg. Chim. Acta*, 1986, **118**, L31.
6 N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, 1974, **15**, 45.
7 J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 1970, 2947.
8 M. K. Cooper, P. A. Duckworth, K. Henrick, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1981, 2357.
9 G. M. Sheldrick, SHELX 76 program system, University of Cambridge, 1976.
10 C. J. Creswell, A. Dobson, D. S. Moore, and S. D. Robinson, *Inorg. Chem.*, 1979, **18**, 2055.
11 D. J. Cole-Hamilton, R. J. Young, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 1995.
12 H. Werner and R. Werner, *J. Organomet. Chem.*, 1980, **194**, C7.
13 B. Bell, J. Chatt, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1973, 997.
14 A. R. Siedle, R. A. Newmark, and L. H. Pignolet, *Inorg. Chem.*, 1986, **25**, 3412.
15 S. M. Boniface, G. R. Clark, T. J. Collins, and W. R. Roper, *J. Organomet. Chem.*, 1981, **206**, 109.
16 P. Bernhard, H-B. Burgi, J. Hauser, H. Lehmann, and A. Ludi, *Inorg. Chem.*, 1982, **21**, 3936.
17 F. Charbonnier, R. Faure, and H. Loiseleur, *Acta Crystallogr., Sect. B*, 1977, **33**, 1845, 3342, and 3759.
18 G. Doyle, K. A. Eriksen, and D. Van Engen, *Inorg. Chem.*, 1983, **22**, 2892.
19 M. B. Humphrey, W. M. Lamanna, M. Brookhart, and G. R. Husk, *Inorg. Chem.*, 1983, **22**, 3355.

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