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Sulphonato Complexes of Ruthenium, Osmium and Iridium; the X-ray Crystal Structure of $Ru(O_3SC_6H_4\text{-}CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2$

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Sulphonate ions, notably $CF_3SO_3^-$, $p\text{-}CH_3C_6H_4SO_3^-$ and $CH_3SO_3^-$ have found extensive use in organic [1, 2] and inorganic [3–7] chemistry as leaving groups and counter anions respectively, but, because of their relatively poor coordinating power, are not commonly encountered as ligands in platinum metal chemistry. In those instances where coordination does occur the sulphonate ligands are usually labile and weakly bound. Sulfphonate complexes of the platinum group metals are therefore of potential interest as catalytic species and synthetic precursors. Indeed several catalytically active platinum metal systems including $Rh_2(O_2CCH_3)_4/CF_3SO_3H$ [8] and $RuH_2(PPh_3)_4/p\text{-}CH_3C_6H_4SO_3H$ [9] employ sulphonic acids, furthermore sulphonate ligands in the complexes $[M(O_3SCF_3)(NH_3)_5]^{2+}$ (M = Ru, Os, Rh or Ir) [5–7] are very susceptible to metathesis.

A recent quickening of interest in transition metal sulphonates and their chemistry [4–7, 10–12] prompts the present preliminary report on the synthesis, structure and reactivity of a range of new platinum group metal sulphonate complexes. The technique used to synthesise the new complexes involves treatment of the appropriate platinum metal hydrides or low oxidation state complexes with the free sulphonic acid $RS(O)_2OH$ (R = CF_3, CH_3, $p\text{-}CH_3C_6H_4$ or d-camphor) in a boiling organic solvent. Brief details of individual syntheses, together with a key (R^1–R^4) to acids used in each, are given in Table I. The new sulphonato complexes have been characterised in solution by ^1H, ^{19}F and ^{31}P NMR, and in most instances have been isolated in good yield as analytically pure, air-stable yellow or white crystalline solids. Many of the products obtained reflect the reluctance of the sulphonate groups to coordinate through oxygen, particularly in bi- or tri-dentate fashion. Thus reactions of sulphonic acids with $RuH_2(PPh_3)_4$ and $OsH_4(PPh_3)_3$ gave the ruthenium(II) [13] and osmium(II) η^6-arene complexes $[MH(\eta^6\text{-}C_6H_6)(PPh_3)_2][O_3SR^1]$ and $[MH(\eta^6\text{-}CH_3C_6H_4SO_3)(PPh_3)_2]$.

In contrast to the corresponding ruthenium reaction, treatment of $OsH_4(PPh_3)_3$ with CF_3SO_3H in ethanol affords a sulphonate salt of the trihydride cation $[OsH_3(PPh_3)_4]^+$, the yield of which is substantially improved by the addition of excess phosphine. Further evidence for the reluctance of sulphonate groups to coordinate in multidentate fashion is provided by reactions of the hydrides RuHCl(CO)-

TABLE I. Synthesis of Ruthenium, Osmium and Iridium Sulphonates

Precursor	Reaction conditions[a]	Product
$RuH_2(PPh_3)_4$	R^1SO_3H, C_6H_6	$[RuH(\eta^6\text{-}C_6H_6)(PPh_3)_2][O_3SR^1]$
	$p\text{-}CH_3C_6H_4SO_3H\cdot H_2O$, C_6H_6	$RuH(\eta^6\text{-}CH_3C_6H_4SO_3)(PPh_3)_2$
$RuH_2(CO)(PPh_3)_3$	RSO_3H, $C_6H_6H_2O$	$Ru(O_3SR)_2(H_2O)(CO)(PPh_3)_2$
$RuHCl(CO)(PPh_3)_3$	R^3SO_3H, 2-MOE, H_2O	$RuCl(O_3SR^3)(H_2O)(CO)(PPh_3)_2$
	CH_3SO_3H, 2-MOE	$RuCl(O_3SCH_3)(CO)(PPh_3)_2$
$Ru(CO)_3(PPh_3)_2$	RSO_3H, C_6H_6	$Ru(O_3SR)_2(CO)_2(PPh_3)_2$
$OsH_4(PPh_3)_3$	R^2SO_3H, C_6H_6	$[OsH(\eta^6\text{-}C_6H_6)(PPh_3)_2][O_3SR^2]$
	$p\text{-}CH_3C_6H_4SO_3H\cdot H_2O$, C_6H_6	$OsH(\eta^6\text{-}CH_3C_6H_4SO_3)(PPh_3)_2$
	CF_3SO_3H, C_2H_5OH	$[OsH_3(PPh_3)_4][O_3SCF_3]$
$OsH_2(CO)(PPh_3)_3$	RSO_3H, C_6H_6	$Os(O_3SR)_2(H_2O)(CO)(PPh_3)_2$
$OsH_2(CO)_2(PPh_3)_2$	R^4SO_3H, C_6H_6	$Os(O_3SR^4)_2(CO)_2(PPh_3)_2$
$OsHCl(CO)(PPh_3)_3$	CH_3SO_3H, 2-MOE	$OsCl(O_3SCH_3)(CO)(PPh_3)_2$
mer-$IrH_3(PPh_3)_3$	R^4SO_3H, C_2H_5OH	$IrH_2(O_3SR^4)(PPh_3)_3$
$IrH(CO)(PPh_3)_3$	RSO_3H, C_6H_6	$[IrH_2(CO)(PPh_3)_3][O_3SR]$
	RSO_3H, $CH_3C_6H_5$	$IrH(O_3SR)_2(CO)(PPh_3)_2$
$IrCl(CO)(PPh_3)_2$	RSO_3H, C_6H_6	$IrHCl(O_3SR)(CO)(PPh_3)_2$

[a] R = CH_3, CF_3, $CH_3C_6H_4$ or d-camphor; R^1 = CH_3, CF_3 or $CH_3C_6H_4$; R^2 = CH_3; CF_3 or d-camphor; R^3 = CH_3 or CF_3; R^4 = $CH_3C_6H_4$ or d-camphor; all reactions under reflux. 2-MOE = 2-methoxy ethanol.

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$(PPh_3)_3$ and $MH_2(CO)(PPh_3)_3$ (M = Ru or Os) with sulphonic acids, in each case traces of water in the solvent lead to the formation of aquo complexes $RuCl(O_3SR)(H_2O)(CO)(PPh_3)_2$ and $M(O_3SR)_2(H_2O)(CO)(PPh_3)_2$ respectively. The X-ray crystal structure of one of these products, $Ru(O_3SC_6H_4CH_3)_2(H_2O)(CO)(PPh_3)_2$ was determined to confirm the stereochemistry and to gain information about the nature of the $Ru-OS(O)_2R$ bond.

Crystal Data

Crystals obtained from dichloromethane/diethyl ether in the presence of traces of water. $C_{51}H_{46}O_8P_2RuS_2$, $M_r = 1014.06$, monoclinic, space group $P2_1/n$, $a = 24.382$, $b = 18.075$, $c = 10.729$ Å, $\beta = 99.03°$, $V = 4652.76$ Å [3], $Z = 4$, $\mu(\text{Mo K}\alpha) = 4.78$ cm^{-1}. The X-ray analysis was performed using 5114 reflections with $I/\sigma(I) \geqslant 3.0$ measured in the θ range 3–25° on a Philips PW1100 four circle diffractometer using Mo Kα radiation from a graphite crystal monochomator. Refinement of positional and thermal parameters for all non-hydrogen atoms was performed using full matrix least-squares procedures [14]. The ruthenium, phosphorus, sulphur and oxygen atoms were assigned anisotropic temperature factors. The phenyl rings were refined as rigid groups (C–C = 1.395 Å). Hydrogen atoms, which were given fixed temperature factors (0.1 Å), were allowed to 'ride' on the carbon atoms in the rings (C–H = 1.08 Å). A final R value of 0.0681 was obtained.

The molecular structure of the complex is shown in Fig. 1, together with selected bond lengths and interatomic distances. The coordination geometry about the ruthenium atom, which is essentially octahedral with two monodentate sulphonates, a coordinated water molecule, a carbonyl group and a pair of triphenylphosphine ligands, closely parallels that previously found [15, 16] for the related carboxylate complex $Ru(O_2CCF_3)_2(CH_3OH)(CO)(PPh_3)_2$. Both complexes adopt sterically unfavorable *cis* arrangements for the bulky triphenylphosphine ligands [<P–Ru–P = 105,0(1)° for sulphonate complex] and both display intramolecular H–bonding interactions between the non-coordinated oxygen atoms of the anionic ligands and the OH groups of water or methanol. Similarities between the two series of complexes extend to their behaviour in solution; the sulphonates, like their carboxylate analogues [15], are fluxional ($^{31}P\{^1H\}$ NMR, low temperature AB pattern coalesces reversibly to singlet on warming) and catalyse the dehydrogenation of primary and secondary alcohols.

The chemical reactivity of the sulphonato complexes further testifies to the good leaving properties of the sulphonate ligands. Carbonylation (CO, C_6H_6, reflux) of the complexes $RuCl(O_3SR^3)(H_2O)(CO)(PPh_3)_2$ and $M(O_3SR)_2(H_2O)(CO)(PPh_3)_2$ affords the *cis*-dicarbonyls $RuCl(O_3SR^3)(CO)_2(PPh_3)_2$ and $M(O_3SR)_2(CO)_2(PPh_3)_2$ respectively. The latter products (M = Ru) react readily with N-donor ligands (L = py, L_2 = dipy, *o*-phen) to form salts $[RuL_2(CO)_2(PPh_3)_2][O_3SR]_2$. The complexes $Ru(O_3SR)_2(H_2O)(CO)(PPh_3)_2$ also react with azobenzene and $Ph_2PCH_2PPh_2$ to form the cyclometallation products $Ru(C_6H_4NNPh)(O_3SR)(CO)(PPh_3)_2$ and the salts *trans*-$[Ru(O_3SR)(CO)(Ph_2PCH_2PPh_2)_2][O_3SR]$ respectively.

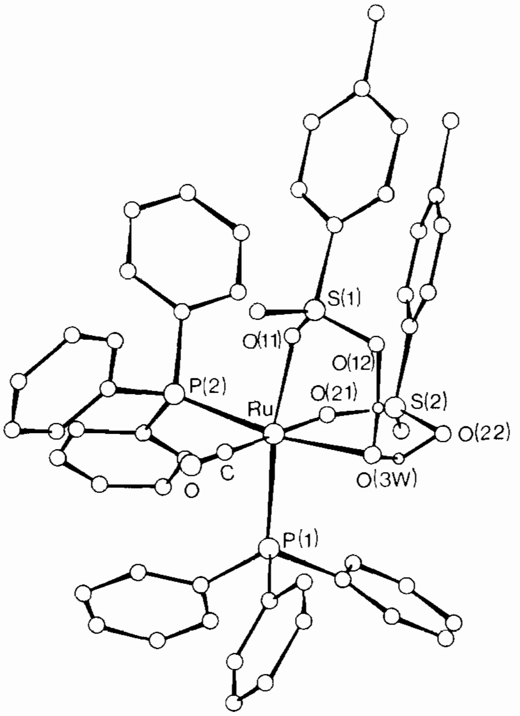

Fig. 1. Molecular structure of $Ru(O_3SC_6H_4CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2$. Selected bond lengths and interatomic distances (Å) are: Ru–P(1) 2.347(2), Ru–P(2) 2.370(2), Ru–C 1.180(9), Ru–O(II) 2.165(5), Ru–O(21) 2.162(6), Ru–I-(3w) 2.202(6), O(3w)...O(12) 2.68, O(3w)...O(22) 2.65.

The iridium(III) sulphonates $IrH_2(O_3SR^4)(PPh_3)_3$ display similar behaviour. They undergo solvation by CH_3CN or C_2H_5OH to afford the salts $[IrH_2(CH_3CN)(PPh_3)_3][O_3SR^4]$ and $[IrH_2(C_2H_5OH)(PPh_3)_3][O_3SR]$ respectively, and react with N-donors to form the salts $[IrH_2L_2(PPh_3)_2][O_3SR^4]$ (*cis* hydrides, *trans* PPh_3 isomers; L = py, γ-picoline, L_2 = dipy *o*-phen, $NH_2CH_2CH_2NH_2$ or *o*-$NH_2C_6H_4NH_2$). Finally carbonylation (CO, C_6H_6, reflux) yields the salts $[IrH_2(CO)(PPh_3)_3][O_3SCF_3]$ and $[Ir(CO)_3(PPh_3)_2][O_3SR^5]$ ($R^5 = CH_3$, *p*-$CH_3C_6H_4$).

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