

Complexes of the Platinum Metals. Part 32.¹ Synthesis and Chemistry of some Iridium Sulphonate Derivatives

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Sulphonic acids RSO_3H ($\text{R} = \text{CF}_3$, CH_3 , or $\text{C}_6\text{H}_4\text{CH}_3$ -*p*) react with *mer*- $[\text{IrH}_3(\text{PPh}_3)_3]$, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, and $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ to afford the products $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$, $[\text{IrH}(\text{Cl})(\text{O}_3\text{SR})(\text{CO})(\text{PPh}_3)_2]$, and $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3][\text{O}_3\text{SR}]$ respectively. Under more vigorous conditions the last reaction yields the bis(sulphonate) complexes $[\text{IrH}(\text{O}_3\text{SR})_2(\text{CO})(\text{PPh}_3)_2]$. The lability of the monodentate sulphonate ligands has been demonstrated by the substitution reactions of $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$ with a variety of neutral donor ligands. Products readily obtained in this manner include $[\text{IrH}_2(\text{CH}_3\text{CN})(\text{PPh}_3)_3][\text{O}_3\text{SR}]$, $[\text{IrH}_2\text{L}_2(\text{PPh}_3)_2][\text{O}_3\text{SR}]$ [$\text{L} = \text{pyridine}$, 4-methylpyridine, or $\text{P}(\text{OPh})_3$; $\text{L}_2 = 2,2'$ -bipyridyl, 1,10-phenanthroline, ethylenediamine, or *o*- NH_2 - $\text{C}_6\text{H}_4\text{NH}_2$], and *trans*- $[\text{IrH}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2][\text{O}_3\text{SR}]$. Carbonylation of $[\text{IrH}_2(\text{O}_3\text{SCF}_3)(\text{PPh}_3)_3]$ affords the tricarbonyl salt $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2][\text{O}_3\text{SCF}_3]$ whereas under similar conditions the precursors $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$ ($\text{R} = \text{CH}_3$ or $\text{C}_6\text{H}_4\text{CH}_3$ -*p*) yield the dihydride salts $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3][\text{O}_3\text{SR}]$. Many of the complexes isolated were solvated by H-bonded molecules of sulphonic acids. Stereochemical assignments based on ^1H , ^{19}F , and ^{31}P n.m.r. data are given for all the new products reported.

Sulphonate ions CH_3SO_3^- , *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ and, in particular, CF_3SO_3^- have found extensive use as leaving groups^{2,3} and counter anions⁴⁻⁸ in organic and inorganic chemistry respectively. However, because of their relatively poor coordinating capacity, they are not commonly encountered as ligands in platinum metal chemistry. In those instances where co-ordination does occur the sulphonate ligands are usually labile and weakly bound.^{4,6-8} Sulphonate 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 $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4]\text{CF}_3\text{SO}_3\text{H}^9$ and $[\text{RuH}_2(\text{PPh}_3)_4]\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}^{10}$ employ sulphonic acids. Furthermore sulphonate ligands in the pentammine complex cations $[\text{M}(\text{O}_3\text{SR})(\text{NH}_3)_5]^{n+}$ ($n = 2$, $\text{M} = \text{Ru}$,⁶⁻⁸ Os ,^{4,6} Rh ,^{6,7} or Ir ;^{6,7} $n = 3$, $\text{M} = \text{Pt}$ ⁷) are susceptible to metathesis.

Previous work on platinum metal sulphonate complexes has largely been restricted to the above-mentioned pentammine salts and some closely related amine,⁷ diamine,⁷ or diimine¹¹⁻¹³ derivatives, notably $[\text{Rh}(\text{O}_3\text{SCF}_3)(\text{NH}_2\text{CH}_3)_5]^{2+}$, $[\text{M}(\text{O}_3\text{SCF}_3)_2(\text{en})_2]^+$ and $[\text{MCl}(\text{O}_3\text{SCF}_3)(\text{en})_2]^+$ ($\text{M} = \text{Rh}$ or Ir , $\text{en} = \text{ethylenediamine}$), $[\text{Ir}(\text{O}_3\text{SCF}_3)_2(\text{bipy})_2]^+$ and $[\text{Ru}(\text{O}_3\text{SCF}_3)_2(\text{CO})_2(\text{L-L})]$ [$\text{L-L} = 2,2'$ -bipyridyl (bipy) or 1,10-phenanthroline (phen)]. The paucity of data on analogous sulphonate complexes containing ancillary phosphine and/or carbonyl ligands prompted us to initiate a study on some systems of this type. In this paper we describe results obtained with iridium. Prior to this investigation studies on the oxidative addition of sulphonic acids and/or sulphonic esters to some iridium(I) complexes, $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$,¹⁴⁻¹⁶ $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$,^{14,17-19} and $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ ²⁰ had led to the isolation of several iridium(III) sulphonate complexes. The present work in addition to confirming and extending these observations, includes details of the substitution patterns displayed by some of the sulphonate complexes isolated. A preliminary account²¹ of our work in this area includes some of the material discussed in the present paper.

A recent review of co-ordinated trifluoromethanesulphonate and fluorosulphate ligands, FSO_3^- , provides a very useful account of previous work in this general area of co-ordination chemistry.²²

Experimental

Iridium salts were supplied by INCO Europe Ltd., and were converted to the phosphine complexes carbonylchlorobis(triphenylphosphine)iridium(I), carbonylhydridotris(triphenylphosphine)iridium(I), and *mer*-trihydridotris(triphenylphosphine)iridium(III) by standard literature procedures.²³ All reactions were performed under nitrogen but products were worked-up in open vessels. Solvents were dried over molecular sieves. Analyses were performed by the Microanalytical laboratory, King's College. Proton and ^{19}F n.m.r. spectra were recorded in CDCl_3 solution at 250 and 235.35 MHz respectively using a Bruker WM 250 spectrometer and are referenced to SiMe_4 and CFCl_3 respectively; ^{31}P n.m.r. were recorded in CDCl_3 solution at 36.44 MHz using a Bruker HFX 90 spectrometer and are referenced to external 85% H_3PO_4 . Positive values for chemical shifts indicate resonances at low field relative to the reference. Infrared spectra were taken on a Perkin-Elmer 983G spectrometer using samples milled in Nujol. Spectroscopic data are presented in Tables 1 and 2.

Dihydrido(trifluoromethanesulphonato)tris(triphenylphosphine)iridium(III)-Trifluoromethanesulphonic Acid (1/1).—A mixture of trifluoromethanesulphonic acid (0.16 cm³, 1.81 mmol) and *mer*- $[\text{IrH}_3(\text{PPh}_3)_3]$ (0.8 g, 0.815 mmol) in ethanol (35 cm³) was heated under reflux to give a colourless solution which turned yellow after 40 min. The solution was cooled, filtered, and concentrated under reduced pressure, and then allowed to stand at room temperature until crystallisation was complete. Filtration followed by washing with diethyl ether and *n*-hexane gave glittering white microcrystals (0.39 g, 37%) (Found: C, 53.15; H, 4.20. $\text{C}_{55}\text{H}_{47}\text{F}_3\text{IrO}_3\text{P}_3\text{S}\cdot\text{CF}_3\text{SO}_3\text{H}$ requires C, 52.55; H, 3.80%).

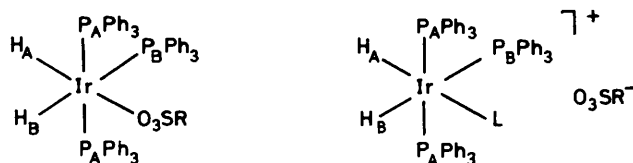
The following were similarly prepared $[\text{IrH}_2(\text{O}_3\text{SCH}_3)(\text{PPh}_3)_3]\cdot\text{CH}_3\text{SO}_3\text{H}$ as white microcrystals (75%) (Found: C, 57.15; H, 4.50. $\text{C}_{55}\text{H}_{50}\text{IrO}_3\text{P}_3\text{S}\cdot\text{CH}_3\text{SO}_3\text{H}$ requires C, 57.35; H, 4.65%) and $[\text{IrH}_2(\text{O}_3\text{SC}_6\text{H}_4\text{CH}_3\text{-p})(\text{PPh}_3)_3]\cdot\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ as white microcrystals (87%) (Found: C, 61.85; H, 5.15. $\text{C}_{61}\text{H}_{54}\text{IrO}_3\text{P}_3\text{S}\cdot\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ requires C, 61.65; H, 4.55%).

Carbonylchlorohydrido(trifluoromethanesulphonato)bis(triphenylphosphine)iridium(III)-Trifluoromethanesulphonic Acid

Table 1. I.r. and n.m.r. data^a for iridium sulphonate complexes

Complex ^b	R	$\nu(\text{IrH})/\text{cm}^{-1}$	$\nu(\text{CO})/\text{cm}^{-1}$	$\delta(\text{IrH})/\text{p.p.m.}$	$J(\text{PH})/\text{Hz}$	$\delta(\text{P})/\text{p.p.m.}$	$\delta(\text{F})/\text{p.p.m.}$
[IrH ₂ (O ₃ SR)(PPh ₃) ₃]	CF ₃	2 287, 2 131	—	← ————— →	See Table 2	← ————— →	-77.7(s)
	CH ₃	2 249, 2 140	—				
	<i>p</i> -C ₆ H ₄ CH ₃	2 242, 2 144	—				
[IrH(Cl)(O ₃ SR)(CO)(PPh ₃) ₂]	CF ₃	2 295	2 060	-21.3(t)	ca. 12	4.8(s)	-76.9(s)
	CH ₃	2 280	2 050	-20.3(t)	ca. 12	4.75(s)	
	<i>p</i> -C ₆ H ₄ CH ₃	2 251	2 056	-20.0(t)	ca. 12	4.8(s)	
[IrH ₂ (CO)(PPh ₃) ₃][O ₃ SR]	CF ₃	2 160, 2 105	2 010	← ————— →	See Table 2	← ————— →	-78.48(s)
	CH ₃	2 160, 2 104	2 003				
[IrH(O ₃ SR) ₂ (CO)(PPh ₃) ₂]	CF ₃	2 297	2 073	-21.5(t)	11.8	13.9(s)	-78.1(s)
	CH ₃	2 273	2 050	-19.6(t)	10.8	8.5(s)	
[IrH ₂ (CH ₃ CN)(PPh ₃) ₃][O ₃ SR]	CF ₃	2 193, 2 113	—	← ————— →	See Table 2	← ————— →	-78.58(s)
	CH ₃	2 200, 2 120	—				
	<i>p</i> -CH ₃ C ₆ H ₄	2 190, 2 114	—				
[IrH ₂ (py) ₂ (PPh ₃) ₂][O ₃ SR]	CF ₃	2 147 ^c	—	-21.63(t)	17.5	23.49(s)	-78.52(s)
	CH ₃	2 174 ^c	—	-21.63(t)	17.5	23.25(s)	
	<i>p</i> -CH ₃ C ₆ H ₄	2 150 ^c	—	-21.62(t)	17.5	23.41(s)	
[IrH ₂ (4Me-py) ₂ (PPh ₃) ₂][O ₃ SR]	CF ₃	2 159, 2 143	—	-21.64(t)	17.6	22.77(s)	-78.56(s)
	<i>p</i> -CH ₃ C ₆ H ₄	2 181, 2 134	—	-21.65(t)	17.6	22.77(s)	
[IrH ₂ (bipy)(PPh ₃) ₂][O ₃ SR]	CF ₃	2 206, 2 179	—	-19.54(t)	16.7	19.96(s)	-78.48(s)
	CH ₃	2 240, 2 155	—	-19.58(t)	16.9	19.62(s)	
	<i>p</i> -C ₆ H ₄ CH ₃	2 150, 2 109	—	-19.58(t)	16.8	19.66(s)	
[IrH ₂ (phen)(PPh ₃) ₂][O ₃ SR]	CF ₃	2 222, 2 167	—	-19.27(t)	16.4	20.87(s)	-78.52(s)
	CH ₃	2 167 ^c	—	-19.27(t)	16.5	20.79(s)	
	<i>p</i> -C ₆ H ₄ CH ₃	2 217, 2 121	—	-19.28(t)	16.4	20.83(s)	
[IrH ₂ (en)(PPh ₃) ₂][O ₃ SR]	CF ₃	2 155 ^c	—	-20.82(t)	17.8	20.95(s)	-78.73(s)
	CH ₃	2 187, 2 123	—	-20.74(t)	17.8	21.10(s)	
	<i>p</i> -C ₆ H ₄ CH ₃	2 164 ^c	—	-20.74(t)	17.8	20.95(s)	
[IrH ₂ (<i>o</i> -NH ₂ C ₆ H ₄ NH ₂)- (PPh ₃) ₂][O ₃ SR]	CF ₃	2 203, 2 170	—	-20.74(t)	16.8	22.77(s)	-78.49(s)
[IrH ₂ (PPh ₃) ₂ {P(OPh) ₃ } ₂][O ₃ SR]	CF ₃	2 125 ^c	—	← ————— →	See text	← ————— →	-78.49(s)
[IrH ₂ (Ph ₂ PCH ₂ PPh ₂) ₂][O ₃ SR]	<i>p</i> -C ₆ H ₄ CH ₃	1 769	—	-7.63(q)	14.2	-50.26(s)	
[Ir(CO) ₃ (PPh ₃) ₂][O ₃ SR]	CH ₃	—	{ 1 985 (sh)	—	—	-3.47(s)	
			{ 2 020, 2 078 (sh)	—	—		
			{ 1 984 (sh)	—	—		
	<i>p</i> -C ₆ H ₄ CH ₃	—	{ 2 007, 2 071 (sh)	—	—	-3.31(s)	

^a s = Singlet, t = triplet, and q = quintet. ^b For details of solvation see Experimental section. ^c Broad unresolved peak.

Table 2. Proton and ³¹P-{¹H} n.m.r. chemical shift (p.p.m.) and coupling constant (Hz) data for [IrH₂(O₃SR)(PPh₃)₃] and [IrH₂L(PPh₃)₃][O₃SR]

R	L	$\delta(\text{H}_A)$	$\delta(\text{H}_B)$	$^2J(\text{H}_A\text{H}_B)$	$^2J(\text{H}_A\text{P}_A)$	$^2J(\text{H}_A\text{P}_B)$	$^2J(\text{H}_B\text{P}_A)$	$^2J(\text{H}_B\text{P}_B)$	$\delta(\text{P}_A)$	$\delta(\text{P}_B)$	$^2J(\text{P}_A\text{P}_B)$
CF ₃	—	-27.4(br e)	-10.8(dtd)	n.r.	n.r.	n.r.	21	128	11.2(d)	5.0(br e)	13.2
CH ₃	—	-28.0(br e)	-9.9(dtd)	ca. 5	n.r.	n.r.	21	133	10.9(d)	5.2(br e)	13.2
<i>p</i> -CH ₃ C ₆ H ₄	—	-27.2(br e)	-10.9(dtd)	ca. 5	n.r.	n.r.	ca. 21	132	11.6(br e)	5.4(br e)	n.r.
CF ₃	CH ₃ CN	-19.9(dtd)	-12.15(dtd)	ca. 5	n.r.	n.r.	20.5	124	8.7(d)	1.6(br e)	13.2
CH ₃	CH ₃ CN	-19.9(dtd)	-12.15(dtd)	ca. 5	n.r.	n.r.	20.5	124	8.2(d)	1.4(br e)	13.2
<i>p</i> -CH ₃ C ₆ H ₄	CH ₃ CN	-19.9(dtd)	-12.15(dtd)	ca. 5	n.r.	n.r.	20.5	124	8.4(d)	1.5(br e)	14.7
CF ₃	CO	-9.6(br e)	-11.4(dtd)	ca. 4.5	n.r.	n.r.	18.5	115	1.1(d)	-1.5(br e)	13.2
CH ₃	CO	-9.6(br e)	-11.4(dtd)	ca. 4.5	n.r.	n.r.	19.5	115	0.7(d)	-1.95(br e)	13.2

br e = Broad envelope, d = doublet and t = triplet; n.r. = not resolved.

(2/1).—A mixture of trifluoromethanesulphonic acid (0.05 cm³, 0.56 mmol) and [IrCl(CO)(PPh₃)₂] (0.2 g, 0.26 mmol) in benzene (6 cm³) was heated under reflux for 1 h to give a pale yellow solution which was cooled, filtered, and then concentrated under reduced pressure to deposit a non-crystalline solid.

Trituration under n-hexane afforded white microcrystals (0.25 g, 95%) (Found: C, 45.35; H, 3.10. C₃₈H₃₁ClF₃IrO₄P₂S_{0.5}CF₃SO₃H requires C, 46.00; H, 3.10%).

The complex [IrH(Cl)(O₃SCH₃)(CO)(PPh₃)₂].0.5CH₃SO₃H was similarly prepared using methanesulphonic acid but

after ca. 30 min reflux the product deposited spontaneously as white crystals (84%) (Found: C, 51.00; H, 4.20. $C_{38}H_{34}ClIrO_4P_2S \cdot 0.5CH_3SO_3H$ requires C, 50.00; H, 3.95%).

The complex $[IrH(Cl)(O_3SC_6H_4CH_3-p)(CO)(PPh_3)_2]$ was similarly prepared using toluene-*p*-sulphonic acid and deposited from solution on cooling as white fibrous crystals which were recrystallised from dichloromethane-*n*-hexane and dried *in vacuo* (80%) (Found: C, 55.35; H, 4.00. $C_{44}H_{38}ClIrO_4P_2S$ requires C, 55.50; H, 4.00%).

Carbonyldihydridotris(triphenylphosphine)iridium(III) Trifluoromethanesulphonate-Trifluoromethanesulphonic acid (1/1).—A mixture of trifluoromethanesulphonic acid (0.08 cm³, 0.873 mmol) and $[IrH(CO)(PPh_3)_3]$ (0.4 g, 0.397 mmol) in benzene (10 cm³) was heated under reflux for 1 h to give a colourless solution which was cooled, filtered, and evaporated under reduced pressure to form a colourless oil. This was reprecipitated from dichloromethane-*n*-hexane as a tacky solid which on trituration under *n*-hexane yielded the product as a light yellow powder (0.35 g, 60%) (Found: C, 52.40; H, 3.80. $C_{56}H_{47}F_3IrO_4P_3S \cdot CF_3SO_3H$ requires C, 52.35; H, 3.70%).

The complex $[IrH_2(CO)(PPh_3)_3][O_3SCH_3] \cdot 2CH_3SO_3H$ was similarly prepared using methanesulphonic acid and was isolated as a light yellow powder (54%) (Found: C, 53.85; H, 4.40. $C_{56}H_{50}IrO_4P_3S \cdot 2CH_3SO_3H$ requires C, 53.75; H, 4.50%).

Carbonyldihydridotris(trifluoromethanesulphonato)bis(triphenylphosphine)iridium(III).—A large excess of trifluoromethanesulphonic acid (0.4 g, 3.97 mmol) was added to a suspension of $[IrH(CO)(PPh_3)_3]$ (0.35 g, 0.397 mmol) in toluene (10 cm³). Immediate decolourisation occurred. The mixture was then heated under reflux for 4 h to give a yellow solution which was cooled, filtered, and then concentrated under reduced pressure to afford white crystals. These were twice recrystallised from dichloromethane-light petroleum (b.p. 60–80 °C), washed with *n*-hexane, and dried *in vacuo* (48%) (Found: C, 44.85; H, 3.25. $C_{39}H_{31}F_6IrO_7P_2S_2$ requires C, 44.85; H, 3.00%).

The complex $[IrH(O_3SCH_3)_2(CO)(PPh_3)_2]$ was similarly prepared using methanesulphonic acid and was isolated from dichloromethane-light petroleum (b.p. 60–80 °C) as white crystals (48%) (Found: C, 50.25; H, 3.90. $C_{39}H_{37}IrO_7P_2S_2$ requires C, 50.05; H, 4.00%).

Dihydrido(methyl cyanide)tris(triphenylphosphine)iridium(III) Trifluoromethanesulphonate-Dichloromethane (2/3).—A solution of $[IrH_2(O_3SCF_3)(PPh_3)_3]$ (0.15 g, 0.13 mmol) in methyl cyanide (10 cm³) was heated under reflux for 1 h. The colourless solution was cooled, filtered, and then evaporated under reduced pressure to yield a colourless oil which was crystallised from dichloromethane-light petroleum (b.p. 60–80 °C). The off-white crystals were washed with diethyl ether and *n*-hexane and then dried *in vacuo* (0.11 g, 61%) (Found: C, 53.75; H, 4.10; N, 1.00. $C_{57}H_{50}F_3IrNO_3P_3S \cdot 1.5CH_2Cl_2$ requires C, 54.10; H, 4.10; N, 1.10%).

The following were similarly prepared: $[IrH_2(CH_3CN)(PPh_3)_3][O_3SCH_3] \cdot 2.5CH_2Cl_2$ as white crystals (39%) (Found: C, 53.40; H, 4.45; N, 1.05. $C_{57}H_{53}IrNO_3P_3S \cdot 2.5CH_2Cl_2$ requires C, 52.85; H, 4.30; N, 1.05%) and $[IrH_2(CH_3CN)(PPh_3)_3][O_3SC_6H_4CH_3-p] \cdot 0.5CH_2Cl_2$ as white crystals (56%) (Found: C, 62.0; H, 4.65; N, 0.90. $C_{63}H_{57}IrNO_3P_3S \cdot 0.5CH_2Cl_2$ requires C, 61.70; H, 4.75; N, 1.15%).

Dihydridotris(pyridine)bis(triphenylphosphine)iridium(III) Trifluoromethanesulphonate.—A solution of $[IrH_2(O_3SCF_3)(PPh_3)_3]$ (0.2 g, 0.18 mmol) in pyridine (py) (10 cm³) was heated under reflux for 1 h. The yellow solution was cooled, filtered, and evaporated under reduced pressure to give an oily yellow solid. Crystallisation from dichloromethane-light petroleum

(b.p. 60–80 °C) followed by washing with methanol and *n*-hexane afforded white crystals (0.12 g, 67%) (Found: C, 55.10; H, 3.90; N, 2.60. $C_{47}H_{42}F_3IrN_2O_3P_2S$ requires C, 55.10; H, 4.15; N, 2.75%).

The following were similarly prepared: $[IrH_2(py)_2(PPh_3)_2][O_3SCH_3]$ as white crystals (90%) (Found: C, 57.85; H, 4.55; N, 2.75. $C_{47}H_{45}IrN_2O_3P_2S$ requires C, 58.20; H, 4.70; N, 2.90%) and $[IrH_2(py)_2(PPh_3)_2][O_3SC_6H_4CH_3-p] \cdot 0.5CH_2Cl_2$ as white crystals (75%) (Found: C, 58.30; H, 4.45; N, 2.30. $C_{53}H_{49}IrN_2O_3P_2S \cdot 0.5CH_2Cl_2$ requires C, 58.90; H, 4.60; N, 2.55%).

Dihydridotris(4-methylpyridine)bis(triphenylphosphine)iridium(III) Trifluoromethanesulphonate.—A mixture of 4-methylpyridine (4Me-py) (0.07 cm³, 0.71 mmol) and $[IrH_2(O_3SCF_3)(PPh_3)_3]$ (0.2 g, 0.18 mmol) in methanol (10 cm³) was heated under reflux for 30 min to give a pale yellow solution. After cooling the solution was evaporated under reduced pressure to yield an oily white solid which was crystallised from dichloromethane-diethyl ether and washed with light petroleum (b.p. 60–80 °C) to give white crystals (0.18 g, 95%) (Found: C, 55.20; H, 4.50; N, 2.50. $C_{49}H_{46}F_3IrN_2O_3P_2S$ requires C, 55.85; H, 4.40; N, 2.65%).

The complex $[IrH_2(4Me-py)_2(PPh_3)_2][O_3SC_6H_4CH_3-p] \cdot 0.5CH_2Cl_2$ was similarly prepared as white crystals (75%) (Found: C, 59.60; H, 5.00; N, 2.40. $C_{55}H_{53}IrN_2O_3P_2S \cdot 0.5CH_2Cl_2$ requires C, 59.60; H, 4.85; N, 2.50%).

(2,2'-Bipyridyl)dihydridotris(triphenylphosphine)iridium(III) Trifluoromethanesulphonate.—A solution of 2,2'-bipyridyl (bipy) (0.16 g, 0.99 mmol) in methanol (10 cm³) was added to a stirred suspension of $[IrH_2(O_3SCF_3)(PPh_3)_3]$ (0.28 g, 0.25 mmol) in methanol (10 cm³) and the whole heated under reflux for 30 min to afford a yellow solution. This was cooled, filtered, and then evaporated under reduced pressure to yield a yellow oil which after twice crystallising from dichloromethane-diethyl ether and washing with diethyl ether and *n*-hexane afforded yellow crystals (0.2 g, 79%) (Found: C, 55.75; H, 4.10; N, 2.45. $C_{47}H_{40}F_3IrN_2O_3P_2S$ requires C, 55.10; H, 3.95; N, 2.75%).

The following were similarly prepared: $[IrH_2(bipy)(PPh_3)_2][O_3SCH_3]$ as yellow crystals (74%) (Found: C, 57.55; H, 4.45; N, 2.75. $C_{47}H_{43}IrN_2O_3P_2S$ requires C, 58.20; H, 4.45; N, 2.90%) and $[IrH_2(bipy)(PPh_3)_2][O_3SC_6H_4CH_3-p]$ as yellow crystals (69%) (Found: C, 60.50; H, 4.50; N, 2.65. $C_{53}H_{47}IrN_2O_3P_2S$ requires C, 60.85; H, 4.55; N, 2.70%).

The following were similarly prepared using 1,10-phenanthroline monohydrate, phen-H₂O, and the appropriate sulphonate complexes: $[IrH_2(phen)(PPh_3)_2][O_3SCF_3]$ as yellow crystals (44%) (Found: C, 55.95; H, 3.60; N, 2.65. $C_{49}H_{40}F_3IrN_2O_3P_2S$ requires C, 56.15; H, 3.85; N, 2.65%), $[IrH_2(phen)(PPh_3)_2][O_3SCH_3] \cdot 0.5CH_2Cl_2$ as yellow crystals (50%) (Found: C, 57.00; H, 4.10; N, 2.80. $C_{49}H_{43}IrN_2O_3P_2S \cdot 0.5CH_2Cl_2$ requires C, 57.35; H, 4.30; N, 2.70%), and $[IrH_2(phen)(PPh_3)_2][O_3SC_6H_4Me-p]$ as yellow crystals (57%) from dichloromethane-light petroleum (b.p. 60–80 °C) (Found: C, 61.60; H, 4.40; N, 2.85. $C_{55}H_{47}IrN_2O_3P_2S$ requires C, 61.85; H, 4.45; N, 2.60%).

(Ethylenediamine)dihydridotris(triphenylphosphine)iridium(III) Trifluoromethanesulphonate.—Ethylenediamine (en) (0.06 cm³, 0.93 mmol) was added to a stirred solution of $[IrH_2(O_3SCF_3)(PPh_3)_3]$ (0.25 g, 0.23 mmol) in benzene (10 cm³) and the mixture heated under reflux for 5 min. The orange-yellow solution was then cooled, filtered, and evaporated under reduced pressure to give an oily residue. This was crystallised from dichloromethane-diethyl ether to yield beige crystals which were washed with diethyl ether and dried *in vacuo* (0.06 g,

29%) (Found: C, 49.85; H, 4.25; N, 3.10. $C_{39}H_{40}F_3IrN_2O_3P_2S$ requires C, 50.45; H, 4.35; N, 3.00%).

The following were similarly prepared using a reflux time of 15 min: $[IrH_2(en)(PPh_3)_2][O_3SCH_3]$ as beige crystals (75%) (Found: C, 53.65; H, 5.00; N, 3.25. $C_{39}H_{43}IrN_2O_3P_2S$ requires C, 53.45; H, 5.25; N, 3.20%) and $[IrH_2(en)(PPh_3)_2][O_3SC_6H_4CH_3-p]$ as beige crystals (73%) (Found: C, 55.95; H, 5.45; N, 3.50. $C_{45}H_{47}IrN_2O_3P_2S$ requires C, 56.90; H, 5.00; N, 2.95%).

Dihydrido(o-phenylenediamine)bis(triphenylphosphine)iridium(III) Trifluoromethanesulphonate.—A solution of *o*-phenylenediamine (0.12 g, 1.11 mmol) in benzene (5 cm³) was added to a stirred solution of $[IrH_2(O_3SCF_3)(PPh_3)_3]$ (0.3 g, 0.27 mmol) in benzene (10 cm³). The mixture was heated under reflux for 15 min to give fibrous white crystals suspended in a blue solution. The crystals were filtered off, washed with diethyl ether, and then recrystallised from dichloromethane–diethyl ether (0.2 g, 77%) (Found: C, 52.45; H, 4.05; N, 2.80. $C_{43}H_{40}F_3IrN_2O_3P_2S$ requires C, 52.90; H, 4.15; N, 2.85%).

cis,cis,cis-Dihydridobis(triphenylphosphine)bis(triphenylphosphite)iridium(III) Trifluoromethanesulphonate–Dichloromethane (1/1).—A solution of triphenyl phosphite (0.2 cm³, 0.73 mmol) and $[IrH_2(O_3SCF_3)(PPh_3)_3]$ (0.2 g, 0.18 mmol) in 2-methoxyethanol (10 cm³) was heated under reflux for 30 min. The clear colourless solution was cooled, filtered, and evaporated under reduced pressure to leave a residual oil which was precipitated from dichloromethane–diethyl ether as a white suspension. Treatment with small volumes of distilled water and diethyl ether gave a white microcrystalline solid which was washed with diethyl ether and light petroleum (b.p. 60–80 °C) and then dried *in vacuo* (0.17 g, 61%) (Found: C, 56.40; H, 4.25; $C_{73}H_{62}F_3IrO_9P_4S \cdot CH_2Cl_2$ requires C, 56.50; H, 4.10%).

Bis[bis(diphenylphosphino)methane]dihydrido-iridium(III) Toluene-p-sulphonate.—Solutions of bis(diphenylphosphino)methane (0.27 g, 0.69 mmol) in benzene (5 cm³) and $[IrH_2(O_3SC_6H_4CH_3-p)(PPh_3)_3]$ (0.2 g, 0.17 mmol) in benzene (8 cm³) were mixed together and heated under reflux for 90 min. The colourless solution was then cooled, filtered, and evaporated under reduced pressure to yield a pale yellow oil which was crystallised from dichloromethane–diethyl ether to give a white powder. Recrystallisation from the same solvents gave white microcrystals (0.05 g, 25%) (Found: C, 60.20; H, 4.50. $C_{57}H_{53}IrO_3P_4S$ requires C, 60.35; H, 4.70%).

Carbonyldihydridotris(triphenylphosphine)iridium(III) Trifluoromethanesulphonate.—Carbon monoxide gas was bubbled through a stirred solution of $[IrH_2(O_3SCF_3)(PPh_3)_3]$ (0.2 g, 0.18 mmol) in benzene (20 cm³) at ambient temperature. Within 5 min white microcrystals were visible in the colourless solution. Passage of carbon monoxide with stirring was continued for 1 h. The precipitated material was then filtered off, washed with *n*-hexane, and recrystallised from dichloromethane–*n*-hexane to afford pale yellow crystals (0.19 g, 90%) (Found: C, 57.80; H, 4.10. $C_{56}H_{47}F_3IrO_4P_3S$ requires C, 58.05; H, 4.10%).

The same product was obtained if the reaction was performed in refluxing benzene.

Tricarbonylbis(triphenylphosphine)iridium(I) Toluene-p-sulphonate–Dichloromethane (2/1).—A stream of carbon monoxide was bubbled through a stirred mixture of $[IrH_2(O_3SC_6H_4CH_3-p)(PPh_3)_3]$ (0.21 g, 0.18 mmol) in benzene (20 cm³) under reflux for 1 h to give a yellow solution, which on cooling deposited white microcrystals. Recrystallisation from dichloromethane–*n*-hexane afforded yellow crystals (0.15 g, 83%) (Found: C, 54.85;

H, 3.95. $C_{46}H_{37}IrO_6P_2S \cdot 0.5CH_2Cl_2$ requires C, 55.45; H, 3.80%).

The complex $[Ir(CO)_3(PPh_3)_2][O_3SCH_3] \cdot 0.5CH_2Cl_2$ was similarly prepared and isolated as pale yellow crystals (38%) (Found: C, 51.45; H, 3.45. $C_{40}H_{33}IrO_6P_2S \cdot 0.5CH_2Cl_2$ requires C, 51.85; H, 3.65%).

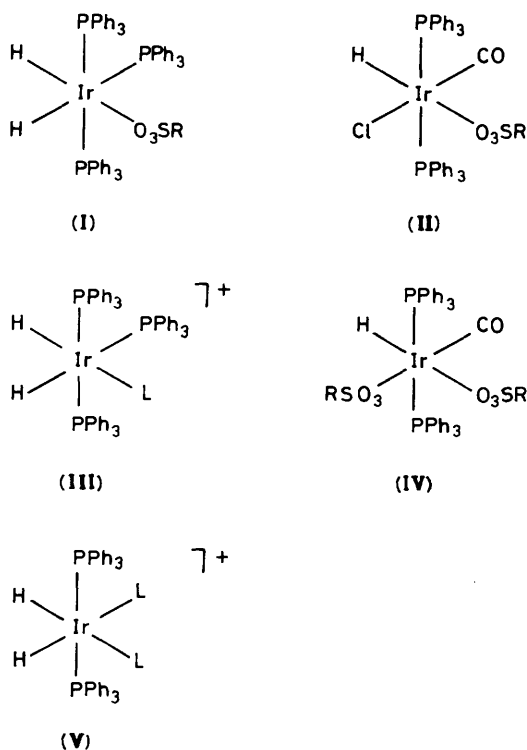
Results and Discussion

This paper is concerned with two aspects of iridium sulphonate chemistry: the synthesis of sulphonate complexes from iridium phosphine precursors and free sulphonic acids, and the substitution reactions of one series of iridium sulphonate derivatives, namely the dihydrides $[IrH_2(O_3SR)(PPh_3)_3]$. The new complexes reported have been characterised by a combination of analytical results and spectroscopic data. Stereochemical assignments have been made largely on the basis of ¹H and ³¹P-¹H n.m.r. spectra. The i.r. spectra, while confirming the presence of the sulphonate ligands (bands at *ca.* 1 350–1 150 cm⁻¹)²² gave little unambiguous evidence concerning structure since the sulphonate bands were partly masked in many instances by other ligand vibrations and, in the case of the trifluoromethanesulphonate complexes, considerable mixing of CF₃ and SO₃ vibrational modes occurs.²⁴

We examine first the synthesis of iridium sulphonate complexes.

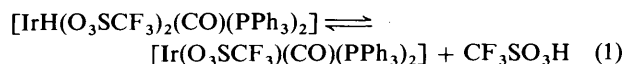
$[IrH_2(O_3SR)(PPh_3)_3] \cdot RSO_3H$ (R = CF₃, CH₃, or C₆H₄-CH₃-*p*).—These white, air-stable crystalline complexes, prepared from *mer*- $[IrH_3(PPh_3)_3]$ and sulphonic acids RSO₃H in refluxing ethanol, are assigned stereochemistry (I) on the basis of i.r. and, in particular, high-field ¹H n.m.r. data (Tables 1 and 2 respectively). A noteworthy feature of the ¹H n.m.r. spectrum is the rather high chemical shift (δ *ca.* –28 p.p.m.) recorded for the hydride ligand *trans* to sulphonate, a value significantly higher than corresponding values (δ *ca.* –23 to –25 p.p.m.) recorded for the analogous carboxylates $[IrH_2(O_2CR)(PPh_3)_3]$.²⁵ This difference no doubt reflects the very low *trans* influence of the weakly co-ordinated sulphonate ligands.²⁶ The additional molecule of sulphonic acid associated with each complex is presumably attached by hydrogen bonding to a non-co-ordinated oxygen atom on the sulphonate ligand. Sulphonic acids are known to participate in hydrogen bonding²⁷ and the i.r. spectra recorded for the present complexes display evidence of such interactions.

$[IrH(Cl)(O_3SR)(CO)(PPh_3)_2]$ (R = CF₃, CH₃, or C₆H₄-CH₃-*p*).—Addition of sulphonic acids to $[IrCl(CO)(PPh_3)_2]$ in benzene leads to rapid formation of solutions which display complex high-field n.m.r. patterns consistent with the presence of several different hydride containing species. However after heating it proved possible to obtain from these solutions good yields of white crystalline complexes $[IrH(Cl)(O_3SR)(CO)(PPh_3)_2] \cdot 0.5RSO_3H$, which on recrystallisation from dichloromethane–*n*-hexane gave the unsolvated products $[IrH(Cl)(O_3SR)(CO)(PPh_3)_2]$. These showed simple ¹H and ³¹P-¹H n.m.r. (Table 1) indicative of pure complexes. The high-field ¹H n.m.r. patterns [δ *ca.* –20 to –21.3 p.p.m. (triplet) ²*J*(PH)_{*cis*} *ca.* 12 Hz] are consistent with hydride *trans* to sulphonate rather than chloride or carbonyl and thus establish stereochemistry (II) for these products. On treatment with polar solvents (CH₃OH, H₂O) loss of sulphonic acid occurs and the original iridium(I) complex $[IrCl(CO)(PPh_3)_2]$ is regenerated. The results obtained in this work are consistent with those reported for an earlier study of the oxidative addition of perfluorosulphonic acids CF₃SO₃H or C₄F₉SO₃H to $[IrCl(CO)(PPh_3)_2]$.^{14,17,18}



$[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3][\text{O}_3\text{SR}] \cdot x\text{RSO}_3\text{H}$ ($\text{R} = \text{CF}_3$, $x = 1$; $\text{R} = \text{CH}_3$, $x = 2$).—These salts, which contain the previously reported²⁰ cation $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^+$, are obtained by treatment of $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ with excess sulphonic acid. A related salt $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3][\text{O}_3\text{SCF}_3]$, which is unsolvated, is also obtained by carbonylation of $[\text{IrH}_2(\text{O}_3\text{SCF}_3)(\text{PPh}_3)_3]$ under mild conditions (see below). The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra confirm the stereochemistry (III; $\text{L} = \text{CO}$) previously established for this cation.²⁰

$[\text{IrH}(\text{O}_3\text{SR})_2(\text{CO})(\text{PPh}_3)_2]$ ($\text{R} = \text{CF}_3$ or CH_3).—These white crystalline complexes were obtained by treatment of $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ with excess sulphonic acid in boiling toluene. The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data (Table 1) are indicative of stereochemistry (IV). The trifluoromethanesulphonate complex has previously been prepared by a similar route but poor analytical data and the absence of any detectable high-field ^1H n.m.r. signal led the earlier workers²⁰ to infer the existence of an oxidative addition–reductive elimination equilibrium [equation (1)].



Substitution Reactions of Complexes $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$.—As noted in the Introduction, our interest in sulphonate complexes stems largely from their ability to serve as synthetic precursors by virtue of the labile, weakly bound nature of coordinated sulphonate anions. We have therefore selected one series of iridium sulphonate complexes and investigated their substitution reactions using a variety of neutral ligands. Since the substitution reactions of complexes $[\text{IrH}(\text{Cl})(\text{O}_3\text{SCF}_3)(\text{CO})(\text{PPh}_3)_2]$ and $[\text{IrH}(\text{Cl})(\text{O}_3\text{SC}_4\text{F}_9)(\text{CO})(\text{PPh}_3)_2]$ have received some attention already^{17,18} and since the stability of the complexes $[\text{IrH}(\text{O}_3\text{SR})_2(\text{CO})(\text{PPh}_3)_2]$ with respect to reductive elimination is in some doubt²⁰ we chose to investigate the dihydride complexes $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$.

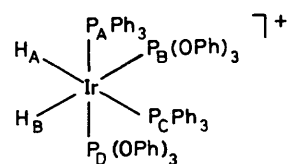


Figure. N.m.r. analysis of $[\text{IrH}_2(\text{PPh}_3)_2\{\text{P}(\text{O}^i\text{Pr})_3\}_2][\text{O}_3\text{SCF}_3]$: $\delta(\text{H}_A) - 12.8$, $\delta(\text{H}_B) - 11.5$, $\delta(\text{P}_A) 0.08$, $\delta(\text{P}_B) 74.12$, $\delta(\text{P}_C) - 0.77$, and $\delta(\text{P}_D) 72.0$ p.p.m.; $^2J(\text{H}_A\text{P}_C)$ ca. 109, $^2J(\text{H}_A\text{P}_B)$ ca. 197, $^2J(\text{H}_B\text{P}_A) = ^2J(\text{H}_B\text{P}_D)$ ca. 20, $^2J(\text{H}_B\text{P}_C)$ ca. 13, and $^2J(\text{H}_A\text{H}_B)$ ca. 4 Hz; other couplings not resolved

Products obtained from reactions of $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$ with nitrogen donor ligands. (i) $[\text{IrH}_2(\text{CH}_3\text{CN})(\text{PPh}_3)_3][\text{O}_3\text{SR}]$. These complex salts were prepared by heating $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$ under reflux in neat methyl cyanide, and were crystallised from dichloromethane–light petroleum as dichloromethane solvates. The $^{31}\text{P}\{-^1\text{H}\}$ and ^1H n.m.r. spectra (Table 2) are consistent with the proposed stereochemistry (III; $\text{L} = \text{MeCN}$). In marked contrast to the situation where pyridine is used as the incoming ligand, there is no evidence for the formation of disubstituted products even using neat methyl cyanide.

(ii) $[\text{IrH}_2\text{L}_2(\text{PPh}_3)_2][\text{O}_3\text{SR}]$ ($\text{L} = \text{py}$ or 4Me-py). These products were obtained as air-stable glittering white crystals by heating $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$ with the appropriate ligand, L , in boiling methanol. The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data (Table 1) are indicative of stereochemistry (V) and the complexes are therefore analogues of the alkene and alkane dehydrogenation agents $[\text{IrH}_2(\text{S})_2(\text{PPh}_3)_2][\text{BF}_4]$ ($\text{S} = \text{solvent}$).²⁸

(iii) $[\text{IrH}_2(\text{L-L})(\text{PPh}_3)_2][\text{O}_3\text{SR}]$ ($\text{L-L} = \text{bipy}$, phen , en , or $o\text{-NH}_2\text{C}_6\text{H}_4\text{NH}_2$). These salts were prepared by heating a mixture of the appropriate precursor $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$ and ligand L-L under reflux in benzene or methanol ($\text{L-L} = \text{bipy}$) and isolated as yellow or beige air-stable crystals. Reactions involving o -phenylenediamine gave rise to a deep blue or purple colouration in the mother-liquor which is being further investigated. The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data (Table 1) for the salts $[\text{IrH}_2(\text{L-L})(\text{PPh}_3)_2][\text{O}_3\text{SR}]$ indicate *cis*-dihydride *trans*-phosphine structures similar to those established above for the closely related bis(pyridine) complexes.

Products obtained from reactions of $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$ with phosphorus donor ligands. (i) $[\text{IrH}_2(\text{PPh}_3)_2\{\text{P}(\text{O}^i\text{Pr})_3\}_2][\text{O}_3\text{SCF}_3]$. This air-stable white crystalline powder was prepared by heating $[\text{IrH}_2(\text{O}_3\text{SCF}_3)(\text{PPh}_3)_3]$ with excess triphenyl phosphite in boiling 2-methoxyethanol. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum displays four sets of resonances of equal intensity indicative of phosphorus nuclei in four different chemical environments: two ($\delta - 0.77$ and 0.08 p.p.m.) attributable to PPh_3 ligands and two ($\delta 72.0$ and 74.12 p.p.m.) assigned to $\text{P}(\text{O}^i\text{Pr})_3$ ligands. The ^1H n.m.r. spectrum shows two distinct high-field n.m.r. patterns. These spectra, an incomplete analysis of which is given in the Figure, clearly establish the *cis,cis,cis* stereochemistry shown therein.

(ii) *trans*- $[\text{IrH}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2][\text{O}_3\text{SC}_6\text{H}_4\text{CH}_3\text{-}p]$. This salt, prepared by heating a mixture of $[\text{IrH}_2(\text{O}_3\text{SC}_6\text{H}_4\text{CH}_3\text{-}p)(\text{PPh}_3)_3]$ and excess $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ under reflux in benzene, is isolated as an air-stable white crystalline solid. The n.m.r. data (Table 1) establish the presence of two equivalent hydride ligands coupled to four equivalent phosphorus nuclei and thus confirm the *trans*-dihydride structure deduced from the i.r. spectrum [$\nu(\text{IrH})$ at 1769 cm^{-1}].

Products obtained from reactions of $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$ with carbon monoxide. (i) $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3][\text{O}_3\text{SCF}_3]$. Carbonylation of $[\text{IrH}_2(\text{O}_3\text{SCF}_3)(\text{PPh}_3)_3]$ in benzene rapidly affords a microcrystalline sample of the known complex

$[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3][\text{O}_3\text{SCF}_3]$ identical with an authentic specimen.²⁰

(ii) $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2][\text{O}_3\text{SR}]$ ($\text{R} = \text{CH}_3$ or $\text{C}_6\text{H}_4\text{CH}_3$ -*p*). In marked contrast to the preceding reaction carbonylation of complexes $[\text{IrH}_2(\text{O}_3\text{SCH}_3)(\text{PPh}_3)_3]$ and $[\text{IrH}_2(\text{O}_3\text{SC}_6\text{H}_4\text{CH}_3\text{-}p)(\text{PPh}_3)_3]$ affords salts of the iridium(i) tricarbonyl cation $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2]^+$. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra consist of a singlet (δ ca. -3.4 p.p.m.) consistent with the expected trigonal bipyramidal *trans*-phosphine structure²⁹ and the i.r. data are in good agreement with those previously reported.³⁰

Differences in behaviour of the complexes $[\text{IrH}_2(\text{O}_3\text{SR})(\text{PPh}_3)_3]$ on carbonylation can be attributed to variations in the lability of the sulphonate ligands. Carbonylation of the trifluoromethanesulphonate leads to rapid displacement of the anionic ligand by carbon monoxide and formation of the stable cation $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^+$ which resists further carbonylation. In contrast carbonylation of the methane- or toluene-*p*-sulphonate salts results in displacement of a phosphine ligand and then the sulphonate anion to afford the dicarbonyl cation $[\text{IrH}_2(\text{CO})_2(\text{PPh}_3)_2]^+$ which, because of the electron-withdrawing power of the *two* carbonyl ligands, readily loses H_2 and adds a third CO to form the observed tricarbonyl cation.³¹

Conclusions

The results reported in this paper clearly establish that iridium phosphine sulphonate complexes are readily accessible and that, by virtue of the labile sulphonate ligands, they are useful precursors for a wide range of iridium complex cations containing a variety of nitrogen, phosphorus, or carbon donor ligands. The potential of the synthetic route is further enhanced by the fact that when ligands of high co-ordinating power are employed the substitution reactions extend beyond displacement of the sulphonate anion to include replacement of one or more of the ancillary phosphine ligands.

Finally the results of the carbonylation reactions clearly demonstrate that small changes in the co-ordinating abilities of the different sulphonate anions can lead to important variation in the pattern of substitution behaviour.

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