Transition-metal Complexes Containing Phosphorus Ligands. Part VIII.[1] Sulphur Dioxide Derivatives of Rhodium, Iridium, Palladium, and Platinum

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The palladium and platinum complexes, $M(PPh_3)_4$, react with sulphur dioxide under anaerobic conditions to afford dark purple air-sensitive derivatives, $M(SO_2)(PPh_3)_3$; these products undergo aerobic oxidation to form sulphato-complexes, $M(SO_4)(PPh_3)_2,H_2O$. The rhodium and iridium hydrides, $M'H(CO)(PPh_3)_3$, on treatment with sulphur dioxide yield the first sulphur dioxide–hydride derivatives, ' $M'H(SO_2)(CO)(PPh_3)_2$ '. The anomalous spectroscopic features of these last-named complexes are tentatively interpreted in terms of a tautomeric equilibrium involving hydride migration between the central metal atom and the co-ordinated sulphur dioxide ligand.

In a previous communication [2] we reported the synthesis of the first palladium and platinum sulphur dioxide derivatives, $M(SO_2)(PPh_3)_3$; detailed discussion of these complexes and some related hydrido(sulphur dioxide) derivatives of rhodium and iridium, ' $M'H(SO_2)(CO)(PPh_3)_2$,' is presented in this paper. The new rhodium and iridium complexes, the first examples containing hydride and sulphur dioxide ligands co-ordinated to the same metal atom, show anomalous spectroscopic features which we tentatively interpret in terms of a rapid tautomeric equilibrium involving the hydride and sulphur dioxide ligands.

Following the publication of our initial study, several groups have reported work on palladium and platinum sulphur dioxide complexes; formation of the species $M(SO_2)(PPh_3)_3$ has been confirmed [3,4] and the new derivatives $M(SO_2)(PPh_3)_4$,[5] $Pt(SO_2)(PPh_3)_2$,[6] $Pt(SO_2)_2(PPh_3)_2$,[4,6] $[PtS(SO_2)(PPh_3)_2]_2$,[7] and $Pt_2Cl_4(SO_2)(PPh_3)_4$ [8] have been described.

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Addition of sulphur dioxide to the square-planar complexes, $M'Cl(CO)(PPh_3)_2$, afforded the first sulphur dioxide derivatives of rhodium and iridium, $M'Cl(SO_2)(CO)(PPh_3)_2$.[9] Other sulphur dioxide complexes of rhodium and iridium subsequently reported are numerous and include, $M'X(SO_2)(CO)(PPh_3)_2$, [M' = Rh, X = F, Br, I, SCN, or NO_3; M' = Ir, X = Br, I, or SPh];[10–12] $[M'(dppe)_2(SO_2)]X$, [X = Cl, Br, or I; dppe = $Ph_2PCH_2CH_2PPh_2$];[12,13] $M'Cl(SO_2)(diene)L$, [L = PPh_3, piperidine],[14] $M'(C{\equiv}CR)(SO_2)(CO)(PPh_3)_2$, [$M'$ = Rh, R = Me or Et; M' = Ir, R = Me, Et, Bu^n, or $C(OH)Me_2$];[15] $RhX(SO_2)(PPh_3)_2$ [X = Cl, Br, or I];[16] $RhCl(SO_2)(CO)_2L$, [L = PPh_3, piperidine];[14] $Rh(\pi\text{-}C_5H_5)(SO_2)(C_2H_4)$;[17] $RhCl_2(\sigma\text{-}C_3H_5)(SO_2)(PPh_3)_2$;[18] $Rh(C_2F_4H)(SO_2)(CO)(PPh_3)_2$,[19] and $IrCl(SO_2)(CS)(PPh_3)_2$.[20] The synthesis of numerous *S*-sulphinate derivatives by 'insertion' of sulphur dioxide into platinum metal–carbon bonds has also been reported.[21]

RESULTS AND DISCUSSION

Platinum.— Tetrakis(triphenylphosphine)platinum, dissolved in benzene, reacted instantly with gaseous sulphur dioxide under anaerobic conditions to form a deep purple solution from which tris(triphenylphosphine)(sulphur dioxide)platinum–benzene solvate crystallised as lustrous dark purple needles. The i.r. spectrum of the new complex showed strong bands characteristic of sym- and asym-sulphur oxygen stretching vibrations (see Table) together with a new band at 677 cm^{-1} attributable to benzene of solvation.[2] The solvent of crystallisation was retained on prolonged pumping (10^{-4} mmHg) at 25°; however on heating *in vacuo* the complex lost benzene above 80° and sulphur dioxide above 110° to yield a solid residue of impure $Pt(PPh_3)_3$. The volatile products were characterised by their gas-phase i.r. spectra and were estimated by thermogravimetric techniques; the latter indicated a ratio of 1 : 1 : *ca.* 1·6 for $Pt(PPh_3)_3$, sulphur dioxide, and benzene respectively.

Infrared data for sulphur dioxide complexes

Complex	$\nu(SO_2)/cm^{-1}$	
	sym	asym
$Pd(SO_2)(PPh_3)_3$	1056s	1215s
$Pt(SO_2)(PPh_3)_3$	1053s	1201s
'$RhH(SO_2)(CO)(PPh_3)_2$'	1038s	1183s
'$IrH(SO_2)(CO)(PPh_3)_2$'	1037s	1175m

On washing thoroughly with diethyl ether the well formed needles of $Pt(SO_2)(PPh_3)_3,xC_6H_6$ crumbled and lost benzene to give the unsolvated complex tris(triphenylphosphine)(sulphur dioxide)platinum as red-brown microcrystals. This product, on heating *in vacuo*, evolved only sulphur dioxide and its i.r. spectrum did not show the band at 677 cm^{-1} previously associated with the presence of benzene solvate molecules. The unsolvated complex was also prepared directly from tetrakis(triphenylphosphine)platinum in toluene solution; presumably, for steric reasons, the larger toluene molecule cannot replace benzene in the crystal lattice. It is interesting to note that exclusion of benzene from the crystal lattice greatly enhanced the aerobic stability of the complex. Thus the solvated crystals oxidised to sulphate completely within 24 h whereas the unsolvated material oxidised slowly over a period of several days. The product obtained from the aerobic oxidation of the platinum–sulphur dioxide complex was identified as sulphatobis(triphenylphosphine)platinum monohydrate. The presence of water molecules within the crystals was indicated by the appearance of broad i.r. bands at 3600—3200 and 1630—1600 cm^{-1}, and was confirmed by analytical data. The oxidised complex showed i.r. bands at 1285—1270, 1175—1160, 890, 880, and 660 cm^{-1} attributable to bidentate sulphato-ligands;[22,23] the water molecule, which appears to be firmly bound, is therefore probably trapped in the lattice or associated with the sulphato group rather than co-ordinated to the platinum atom.

The complex, $Pt(Ph_2PCH_2CH_2PPh_2)_2$, also reacted instantly with sulphur dioxide in benzene under anaerobic conditions to give a dark purple solid; however on exposure to air immediate oxidation of the complex to a white powder occurred. The sulphur dioxide complex was too air-sensitive and the white, oxidised solid too intractable for either to be characterised.

Palladium.—Tris(triphenylphosphine)(sulphur dioxide)palladium was readily prepared by reaction of sulphur dioxide with tetrakis(triphenylphosphine)palladium in benzene under anaerobic conditions, and deposits from solution rapidly as red microcrystals. The complex, isolated in this manner, contains no solvent of crystallisation and on heating to 120° *in vacuo* decomposes with evolution of sulphur dioxide alone. In the solid state the palladium complex is less air-sensitive than its unsolvated platinum analogue and undergoes aerobic oxidation only over a period of weeks; in solution, however, oxidation to the known sulphato-complex $Pd(SO_4)(PPh_3)_2,H_2O$ occurs rapidly. The palladium

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sulphato-complex was characterised by analysis and by i.r. spectroscopy [ν(SO_4) 1245, 1160—1145, 895, 885, and 645 cm^{-1}].[22]

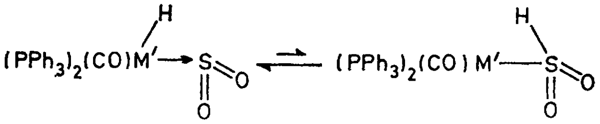
The palladium complex, $Pd(Ph_2PCH_2CH_2PPh_2)_2$, like its platinum analogue, reacts with sulphur dioxide; however the resultant complex is too air-sensitive to isolate and the oxidised products are too intractable to characterise.

Following our preliminary communication of this study Kashiwagi *et al.* reported [5] the reaction of sulphur dioxide with the complexes $M(PPh_3)_4$ [M = Pd or Pt] under conditions similar to those employed in the present work and described products apparently identical with those discussed above. However these workers did not report the presence of any benzene solvate molecules and, on the basis of their analytical data, formulated the products as tetrakis(triphenylphosphine) derivatives, $M(SO_2)(PPh_3)_4$.[5] The analytical data and thermal decomposition studies reported in the present paper support our original formulation [2] of the sulphur dioxide complexes as tris(triphenylphosphine) derivatives. Moreover this conclusion is supported by *X*-ray fluorescence measurements, using $Pt(PPh_3)_3$ and $Pt(PPh_3)_4$ as standards, which confirm a Pt : P ratio of 1 : 3 for the benzene solvated platinum–sulphur dioxide complex.

Iridium and Rhodium.—The iridium and rhodium complexes, $M'H(CO)(PPh_3)_3$ [M′ = Ir or Rh], dissolved in liquid sulphur dioxide to form lime-green and orange-yellow solutions respectively. On concentrating and cooling these solutions, crystals of the lime-green iridium complex '$IrH(SO_2)(CO)(PPh_3)_2$' and its orange-yellow rhodium analogue, '$RhH(SO_2)(CO)(PPh_3)_2$' were deposited. The same products were obtained more conveniently by bubbling sulphur dioxide through n-hexane suspensions of the complexes, $M'H(CO)(PPh_3)_3$. These new hydrides, the first examples containing hydride and sulphur dioxide ligands co-ordinated to the same metal atom, cannot be characterised fully by spectroscopic methods for reasons discussed below, and were therefore identified by chemical means. The complexes are monomeric and have ν(SO_2) and ν(CO) frequencies, colours, and physical properties similar to those recorded by Wilkinson *et al.* for the corresponding sulphur dioxide–acetylide derivatives, $M'(C{\equiv}CR)(SO_2)CO(PPh_3)_2$;[15] on treatment with excess triphenylphosphine in cold benzene they lose sulphur dioxide and regenerate the parent hydrides. On the basis of this evidence the new complexes are formulated as sulphur dioxide–hydride derivatives, $M'H(SO_2)(CO)(PPh_3)_2$ even though the hydride ligands cannot be unambiguously detected by spectroscopic means. The sulphur dioxide–hydride complexes are stable to air for periods of several days; on attempting to oxidise the co-ordinated sulphur dioxide ligands with molecular oxygen in benzene solution only intractable products were obtained; similar oxidations of other rhodium and iridium sulphur dioxide complexes $M'X(SO_2)(CO)(PPh_3)_2$ [X = Cl, Br, I, C≡CR, or SPh] have been reported to afford sulphato-derivatives.[11,23]

Spectroscopic and Structural Features.—The i.r. spectra of the new sulphur dioxide complexes contain bands attributable to sym- and asym-stretching vibrations of a sulphur dioxide group (see Table); the frequencies are similar in value for each complex and are consistent with the presence of a sulphur dioxide moiety co-ordinated to the metal either in a non-planar fashion (as a σ-acceptor ligand) or possibly as part of an *S*-sulphinato-[$-S(O)_2R$] ligand. The rhodium and iridium derivatives $M'H(SO_2)(CO)(PPh_3)_2$ show carbonyl stretching vibrations in their i.r. spectra at 2065vs and 2050vs cm^{-1} respectively; corresponding ν(CO) frequencies for the acetylide complexes $M'(C{\equiv}CR)(SO_2)(CO)(PPh_3)_2$ have been reported to occur at *ca.* 2011s and 2027s cm^{-1}. The i.r. spectrum of the iridium complex also contains a strong sharp band at 1965 cm^{-1} which we attribute to ν(IrH). No absorption attributable to ν(RhH) was visible in the i.r. spectrum (Nujol mull) of the rhodium analogue, however spectra of this complex taken in chloroform contained an extra weak band at 2020 cm^{-1} which may correspond to the 'missing' rhodium hydride vibration. High field n.m.r. spectra, taken over the temperature range (+25 to −60°) using a computer of average transients to improve the signal to noise ratio, failed to reveal any evidence for the presence of co-ordinated hydride ligands in either the rhodium or the iridium complex.

To account for the absence of discernible high-field n.m.r. signals, we tentatively suggest that the rhodium and iridium complexes $M'H(SO_2)(CO)(PPh_3)_2$ exist in solution as labile tautomeric equilibrium mixtures:



The proposed equilibrium process, which is essentially a hydride migration between the central metal ion and the co-ordinated sulphur dioxide ligand, is similar to the aryl and alkyl migration processes postulated for sulphur dioxide and carbon monoxide 'insertion' and 'elimination' reactions.* Insertion of sulphur dioxide into

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* In an apparently related series of reactions Wilkinson *et al.*[24] have observed spectral evidence consistent with the oxidative addition and hydride transfer sequence:

$$IrH(CO)(PPh_3)_3 + CS_2 \longrightarrow IrH(\pi CS_2)(CO)(PPh_3)_2 + PPh_3$$
$$\longrightarrow Ir(CS_2H)(CO)(PPh_3)_2$$

Metal to ligand hydrogen transfer reactions involving nitrosyl,[25] ketimido,[26] and acetylene [27] ligands are also known. *Note added in proof*: Rearrangement of indium(III) *S*-sulphinato-complexes under mild conditions to form corresponding alkyl and aryl $IrCl_2R(SO_2)(PPh_3)_2$ complexes has recently been reported (M. Kubota and B. M. Loeffler, *Inorg. Chem.*, 1972, **11**, 469).

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Group VIII metal–carbon bonds is known to give the *S*-sulphinate [$-S(O)_2R$] group in the majority of instances;[21] accordingly, while not eliminating the alternative forms $-OS(O)H$ or $-S(O)OH$, we favour the structure $-S(O)_2H$ for the postulated $-SO_2H$ ligand.

The iridium complex shows an i.r. band at *ca.* 1965 cm^{-1}, in the solid state and in solution, attributable to ν(IrH) and therefore presumably exists predominantly as the hydrido-iridium species $IrH(SO_2)(CO)(PPh_3)_2$. The unusually low value observed for ν(IrH) may be a further indication of some form of interaction between the hydride and sulphur dioxide ligands in the iridium complex. A similar interaction between the hydroxyl groups of co-ordinated acetylenes, $HOCR_2{\cdot}C{\equiv}C{\cdot}CR_2OH$, and the central platinum ion in $[PtCl_3(HOCR_2{\cdot}C{\equiv}C{\cdot}CR_2OH)]^-$ has been suggested to account for a lowering of ν(OH) by *ca.* 110—140 cm^{-1} on co-ordination.[28] The structure of the rhodium complex '$RhH(SO_2)(CO)(PPh_3)_2$' is more open to speculation: if a band arising from ν(RhH) is present and is concealed beneath the ν(CO) band at *ca.* 2065 cm^{-1} then the structure $RhH(SO_2)(CO)(PPh_3)_2$ is the more appropriate one; alternatively in the absence of bands attributable to ν(OH) [*ca.* 3650—3200 cm^{-1}], ν(SH) [2600—2400 cm^{-1}], or ν(RhH) we cannot distinguish between the structures $RhH(SO_2)(CO)(PPh_3)_2$ and $Rh(SO_2H)(CO)(PPh_3)_2$ postulated above. As noted previously, the i.r. frequencies ν(SO_2) recorded for the rhodium and iridium derivatives are compatible with the presence of either $-SO_2$ or $-SO_2H$ ligands and thus do not afford a means of distinguishing between the tautomeric forms proposed for these complexes.

EXPERIMENTAL

Platinum metal salts were obtained from Johnson Matthey; sulphur dioxide was purchased from B.D.H., dried using conc. sulphuric acid, and used without further purification. All reactions involving sulphur dioxide were performed under nitrogen using oxygen free solvents. Triphenylphosphine and bis(diphenylphosphino)ethane complexes of the platinum metals were prepared by standard literature methods. M.p.s were determined using a Kofler hot stage microscope, unless otherwise specified. I.r. spectra were obtained in Nujol mulls. Molecular weight measurements were taken at 37° using a mechrolab osmometer. Microanalyses were by Dr. Strauss, Oxford.

Tris(triphenylphosphine)(sulphur dioxide)platinum(0) *Benzene Solvate*, $Pt(PPh_3)_3SO_2,xC_6H_6$ (x = 1·5—2·0).—Tetrakis(triphenylphosphine)platinum(0) (1·0 g) was dissolved in cold benzene (20 ml). The solution was filtered and treated with a stream of sulphur dioxide whereupon a deep purple colour developed immediately. After *ca.* 5 min passage of sulphur dioxide was terminated and the solution cooled at 5° for 24 h. The required product, which crystallised from the solution on cooling, was filtered off, washed with benzene (2 × 3 ml), and dried *in vacuo* as *dark purple needles* (0·45 g). Decomp. above 100° when sealed under nitrogen (Found: C, 66·45; H, 4·6. $C_{66}H_{57}O_2P_3PtS$ requires C, 65·95; H, 4·80%).

Tris(triphenylphosphine)(sulphur dioxide)platinum(0), $Pt(PPh_3)_3SO_2$.—Tetrakis(triphenylphosphine)platinum(0) (1·0 g) was dissolved in cold toluene (20 ml). The solution was filtered then treated with sulphur dioxide for 5 min; the resultant dark red-brown solution was cooled at 5° for 16 h. The required product, which crystallised from the cooled solution, was filtered off, washed with toluene, and dried *in vacuo* as *red-brown microcrystals* (0·36 g). Decomp. above 100° when sealed under nitrogen (Found: C, 61·7; H, 4·4; P, 8·65; S, 3·45. $C_{54}H_{45}O_2P_3PtS$ requires C, 62·0; H, 4·35; P, 8·9; S, 3·1. $C_{72}H_{60}O_2P_4PtS$ requires C, 66·1; H, 4·6; P, 9·45; S, 2·45%).

Crystals of the benzene solvated complex $Pt(PPh_3)_3SO_2,xC_6H_6$ fractured and lost benzene on thorough washing with diethyl ether to give the solvent free complex $Pt(PPh_3)_3SO_2$ identical with the above (Found: C, 61·9; 62·15; H, 4·4, 4·35%).

Reaction of Tris(triphenylphosphine)(sulphur dioxide)platinum with Molecular Oxygen and Formation of Sulphatobis(triphenylphosphine)platinum(II) *Monohydrate.*—A stream of sulphur dioxide was passed through a solution of tetrakis(triphenylphosphine)platinum(0) (0·50 g) in benzene (15 ml) for 5 min, the resultant dark purple solution was then exposed to air and was observed to turn pale yellow over a period of hours. After 3 days the required sulphato-complex was filtered off and recrystallised from chloroform–light petroleum (b.p. 40—60°) as *white microcrystals* (0·28 g), m.p. 214—216° with decomp. (Found: C, 51·55; 51·55; H, 3·85, 3·75; S, 3·5, 3·65; P, 7·35%. *M*, 837. Calc. for $C_{36}H_{32}O_5P_2PtS$: C, 51·85; H, 3·85; S, 3·85; P, 7·45%. *M*, 834).

Tris(triphenylphosphine)(sulphur dioxide)palladium(0), $Pd(PPh_3)_3SO_2$.— Tetrakis(triphenylphosphine)palladium(0) (1·0 g) was dissolved in cold benzene (20 ml). The solution was filtered then saturated with a stream of sulphur dioxide whereupon a dark red colour developed instantly. After *ca.* 5 min passage of sulphur dioxide was terminated and the solution was cooled at 5° for 16 h. The required product crystallised, and was filtered off, washed with benzene (2 × 3 ml), then dried *in vacuo* as *dark red microcrystals* (0·45 g). Decomp. above 90° when sealed under nitrogen (Found: C, 67·85; 67·65; H, 4·7, 4·75; P, 10·05, 9·65; S, 3·15. $C_{54}H_{45}O_2P_3PdS$ requires C, 67·75; H, 4·75; P, 9·7; S, 3·35. $C_{72}H_{60}O_2P_4PdS$ requires C, 70·9; H, 4·95; P, 10·15; S, 2·6%). The complex undergoes aerial oxidation only slowly in the solid state and is unchanged on washing thoroughly with diethyl ether (Found: C, 68·0; H, 5·0%).

Reaction of Tris(triphenylphosphine)(sulphur dioxide)palladium with Molecular Oxygen and Formation of Sulphatobis(triphenylphosphine)palladium(II) *Monohydrate.*—A solution of tetrakis(triphenylphosphine)palladium(0) (0·5 g) in benzene (15 ml) was saturated with sulphur dioxide and the resultant red-brown solution was exposed to the atmosphere. After 3 days the required complex was filtered off and recrystallised from chloroform–ethanol as *yellow microcrystals* (0·27 g), m.p. 155° with decomp. (Found: C, 58·15; H, 3·8; P, 8·55; S, 4·1%. *M*, 744. Calc. for $C_{36}H_{32}O_5P_2PdS$: C, 58·0; H, 4·35; P, 8·3; S, 4·3%. *M*, 745).

Hydridocarbonyl(sulphur dioxide)bis(triphenylphosphine)rhodium.—*Synthesis in liquid sulphur dioxide.* Hydridocarbonyltris(triphenylphosphine)rhodium (0·4 g) was suspended in diethyl ether (2 ml) contained in a trap cooled in carbon dioxide–acetone. Sulphur dioxide (*ca.* 25 ml) was condensed into the trap which was then slowly warmed to

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[28] J. Chatt, L. A. Duncanson, and R. G. Guy, *Nature*, 1959, **184**, 526.

$-10°$. The orange solution was allowed to evaporate in a stream of nitrogen until the volume was reduced by *ca.* 60%, then cooled to $-70°$. The required product crystallised and was filtered off then washed with diethyl ether to afford *orange-yellow microcrystals* (0·2 g). I.r. spectrum (Nujol) ν(CO), 2050 cm^{-1}, ν(RhH) not observable (Found: C, 61·8; H, 4·5; S, 4·0%. *M*, 773, 740. $C_{37}H_{31}P_2O_3RhS$ requires C, 61·65; H, 4·35; S, 4·45%. *M*, 720·6).

Synthesis in n-hexane suspension. Hydridocarbonyltris-(triphenylphosphine)rhodium (0·75 g) was suspended in n-hexane (30 ml) and treated with a slow stream of sulphur dioxide for 1 h. The suspension was filtered and the precipitate washed with diethyl ether to give the required product as orange-yellow microcrystals (0·55 g), identical with an authentic specimen.

Conversion of Hydridocarbonyl(sulphur dioxide)bis(triphenylphosphine)rhodium to Hydridocarbonyltris(triphenylphosphine)rhodium.—Hydridocarbonyl(sulphur dioxide)bis-(triphenylphosphine)rhodium (0·15 g) and triphenylphosphine (0·2 g) were suspended in cold benzene (10 ml), and the mixture purged with a slow steam of nitrogen for 10 min. The resultant yellow solution was evaporated *in vacuo* and the residue triturated with methanol. The solid remaining was filtered off, washed repeatedly with diethyl ether, and then identified by i.r. spectroscopy as $RhH(CO)(PPh_3)_3$ [ν(CO) 1918vs; ν(RhH) 2041s cm^{-1}].

Hydridocarbonyl(sulphur dioxide)bis(triphenylphosphine)-iridium.—Synthesis in liquid sulphur dioxide. Hydridocarbonyltris(triphenylphosphine)iridium (0·4 g) was suspended in diethyl ether (2 ml) contained in a trap cooled in carbon dioxide–acetone. Sulphur dioxide (*ca.* 25 ml) was condensed in the trap which was then allowed to warm slowly to $-10°$. The lime-green solution was allowed to evaporate in a stream of nitrogen until the volume was reduced by *ca.* 60%, then cooled to $-70°$. The required product crystallised and was filtered off then washed with diethyl ether to afford *lime-green crystals* (0·26 g). I.r. spectrum (Nujol) ν(CO) 2065vs, ν(IrH) 1965s cm^{-1} (Found: C, 55·15; H, 3·95%. *M*, 841. $C_{37}H_{31}IrO_3P_2S$ requires C, 54·9; H, 3·85%. *M*, 809).

Synthesis in n-hexane suspension. Hydridocarbonyltris-(triphenylphosphine)iridium (0·6 g) was suspended in n-hexane (30 ml) and treated with a slow stream of sulphur dioxide for 1 h. The suspension was filtered and the precipitate washed with diethyl ether to give the required product as lime-green microcrystals (0·4 g), identical with an authentic specimen.

Conversion of Hydridocarbonyl(sulphur dioxide)bis(triphenylphosphine)iridium to Hydridocarbonyltris(triphenylphosphine)iridium.—Hydridocarbonyl(sulphur dioxide)bis-(triphenylphosphine)iridium (0·25 g) and triphenylphosphine (0·2 g) were suspended in cold benzene (10 ml), and the mixture purged with a slow stream of nitrogen for 10 min. The resultant pale yellow solution was evaporated *in vacuo* and the residue triturated with methanol. The solid remaining was filtered off, washed repeatedly with diethyl ether, and then identified by i.r. spectroscopy as $IrH(CO)(PPh_3)_3$ [ν(CO) 1915vs; ν(IrH) 2125s cm^{-1}].

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