

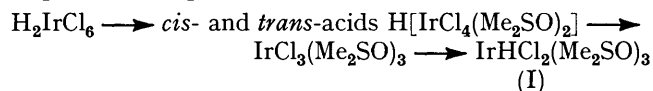
Aspects of Catalysis. Part II.¹ Dimethyl Sulphoxide Complexes of Iridium(III) including Hydrides

By Yousif M. Y. Haddad, H. Bernard Henbest,* and Jadwiga Trocha-Grimshaw, Department of Chemistry, Queen's University, Belfast BT9 5AG

Various dimethyl sulphoxide complexes of iridium(III) have been prepared, including the catalytically active dichlorotris(dimethyl sulphoxide)hydrido-iridium (I), and structures have been assigned.

THE following two papers are concerned with hydrogen transfer reactions catalysed by soluble iridium complexes containing chlorine and dimethyl sulphoxide groups. (A previous paper described a reaction in

which a soluble iridium-phosphite species functioned as the catalyst.¹) The preparation of the dimethyl sulphoxide compounds can be summarised as follows:



¹ Part I, H. B. Henbest and T. R. B. Mitchell, *J. Chem. Soc. (C)*, 1970, 785.

Acids.—The orange-pink *trans*-acid was obtained in high yield by reduction of hexachloroiridic acid in propan-2-ol at 55° (to give the more reactive Ir^{III} species), followed by treatment of the resultant solution with dimethyl sulphoxide at 20°. The acid separated as a crystalline dimethyl sulphoxide solvate $[\text{H}(\text{Me}_2\text{SO})_2]^+[\text{IrCl}_4(\text{Me}_2\text{SO})_2]^-$. Crystalline collidine and isoquinoline salts, $\text{R}_3\text{NH}[\text{IrCl}_4(\text{Me}_2\text{SO})_2]$, were readily prepared.

The yellow *cis*-acid was obtained (together with an easily separated neutral complex; see later) when hexachloroiridic acid was heated in aqueous dimethyl sulphoxide at 95° for 24 h. It also crystallised as a dimethyl sulphoxide solvate in the presence of this solvent, and gave crystalline collidine and isoquinoline salts different from those from the *trans*-acid.

The i.r. spectra of the acids and their salts were in keeping with *S*- and not *O*-bonding² of the sulphoxide groups to iridium in the anions. N.m.r. spectra provided evidence for the *cis*- and *trans*-configurations. The methyl resonance of the orange-pink acid occurs at higher field, closer to the value for uncomplexed dimethyl sulphoxide. This suggests that this acid is the *trans*-form, in which there is less chance for the SO bond of the other ligand to influence the SMe resonance. [Of the two platinum complexes, $\text{Cl}_2\text{Pt}(\text{SOMe})(\text{SMe}_2)$, the *trans*-form has the SMe resonance at higher field than the *cis*-compound.³] The solvent-dependence of the position of equilibrium between the two acids appears to be in keeping with these assignments. The yellow (more polar, *cis*) acid is more stable in aqueous dimethyl sulphoxide solution, whereas in methanol the orange-pink (*trans*) acid is more stable.

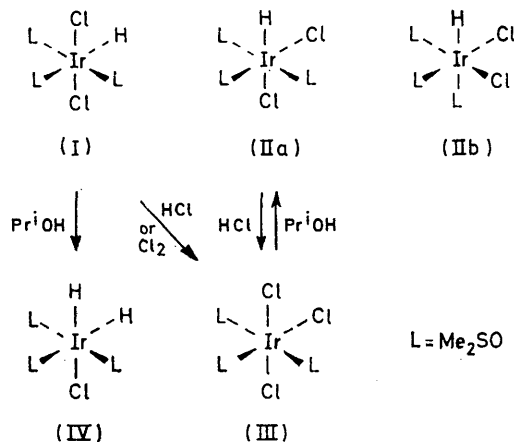
Neutral Complexes.—The pale yellow compound accompanying the *cis*-acid was also obtained by heating iridium tetrachloride with an excess of dimethyl sulphoxide, preferably under oxygen. Analytical and mass spectral information showed that the compound had the constitution $\text{IrCl}_3(\text{Me}_2\text{SO})_3$. The i.r. spectrum showed that two of the sulphoxide molecules are *S*-bonded to iridium and one *O*-bonded; the n.m.r. spectrum showed three separate Me_2SO signals. The stereochemical structure of this substance cannot be assigned with certainty at present. An isomeric compound (III) in which all three sulphoxide ligands are *S*-bonded is discussed later.

Hydrido-iridium complexes containing phosphine, arsine, or stibine ligands have been made⁴ by reduction of appropriate chloro-compounds with hydrazine or sodium borohydride.⁴ These reagents did not prove suitable for obtaining hydrides from the foregoing acidic and neutral sulphoxide complexes. Crystalline hydrides were obtained, however, by using propan-2-ol as reductant (and solvent). Mixtures of products were generally formed, and conditions for obtaining a reasonable yield of a particular substance were critical.

² F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986; F. A. Cotton, R. Francis and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.

³ W. McFarlane and R. F. M. White, *Chem. Comm.*, 1969, 439.

A hydride, $\text{IrHCl}_2(\text{Me}_2\text{SO})_3$, was obtained in 50–60% yield by heating a solution of the *trans*-acid at 55° in slightly aqueous propan-2-ol containing dimethyl sulphoxide (1 mol per mol of acid). This compound showed i.r. bands at 833 and 2190 cm^{-1} . A similar experiment with the *cis*-acid gave an isomeric, more soluble hydride showing i.r. bands at 813 and 2180 cm^{-1} . X-Ray⁵ and n.m.r. evidence shows that the former hydride has structure (I); the HIr signal is at τ 35.3 and the methyl peaks are in a 2:1 intensity ratio. The isomeric hydride from the *cis*-acid showed the HIr resonance at τ 28.8 and three equally intense methyl peaks. It must therefore have structure (IIa) or (IIb), the former being preferred on the following grounds. The compound readily reacted with chlorine in chloroform or hydrogen chloride in ethanol to give a complex (III) in which the three sulphoxide groups remained *S*-bonded. [The structure (III) also follows from its n.m.r. spectrum, which shows two methyl peaks in a 2:1 ratio, the stronger one being at higher field.] In propan-2-ol, the complex (III) was reduced to the hydride (IIa) at an appreciable rate even at room temperature. The hydride (I) reacted with hydrogen chloride in ethanol to give approximately equal amounts of the complex (III) and the *trans*-acid, $\text{H}[\text{IrCl}_4(\text{Me}_2\text{SO})_2]$. Reactions between iridium hydrides (phosphine complexes) and hydrogen chloride have been shown in general to proceed without rearrangement of other ligands,⁶ *cf.*



the foregoing relationships between the sulphoxide compounds. Also, a hydride group can have a *trans*-weakening effect so that a side reaction is replacement of a *trans*-ligand by chloride, *cf.* the formation of some *trans*-acid from the complex (I) and hydrogen chloride.

A mixture of the hydrides (I) and (IIa) was also obtained by heating the complex $\text{IrCl}_3(\text{Me}_2\text{SO})_3$ (in which one ligand is *O*-bonded) in propan-2-ol containing 2% water. The presence of more water (10%) led to

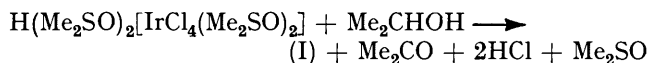
⁴ M. Angoletta, *Gazzetta*, 1962, **92**, 811; A. Araneo, S. Martinego, P. Pasquale, and F. Zingales, *ibid.*, 1965, **95**, 825.

⁵ M. McPartlin and R. Mason, *J. Chem. Soc. (A)*, 1970, 2205.

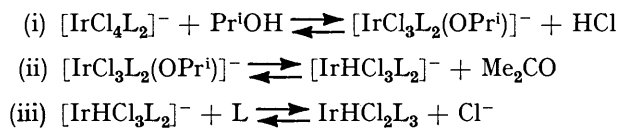
⁶ J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7391

formation of an almost colourless dihydride, $\text{IrH}_2\text{Cl}(\text{Me}_2\text{SO})_3$, which was also obtained from the hydride (I) under the same conditions. The dihydride shows three methyl resonance of equal intensity and two HIr resonances at τ 26.3 and 29.5, each a doublet with J 5.9 Hz. Structure (IV) is therefore assigned.

Hydrogen-Deuterium Exchange in the Complex (I).—Acetone was formed in reactions where propan-2-ol was used as a reductant to prepare the hydride (I) from one of the acids:



Possible mechanistic steps for the reaction are ($\text{L} = \text{Me}_2\text{SO}$):



In previous work on the formation of hydrido-iridium phosphine complexes by reduction of chloro-compounds with ethanol or ethoxide in ethanol it was shown⁷ by using deuteriated solvent ($\text{CH}_3\cdot\text{CD}_2\cdot\text{OH}$) that hydrogen was transferred to iridium from C-1 and not the OH system. This method for determining the origin of the transferred hydrogen was not applicable to the formation of the sulphoxide hydride (I), because this compound readily undergoes deuterium (or hydrogen) exchange in protic (or *O*-deuterium-containing) solvents: thus exchange (to give IrDCl_2L_3) was essentially complete when the hydride (I) was kept in deuterium oxide at 70° for 1 h. This result, together with the ease with which the sulphoxide hydride (I) reacts with $\alpha\beta$ -unsaturated ketones (*cf.* Part IV), suggests that the iridium-hydride bond in (I) is appreciably polarised ($\delta^-\text{Ir}-\text{H}^{\delta+}$), more so than in the less reactive phosphine complexes.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded on a Perkin-Elmer 137 double-beam spectrometer. ¹H N.m.r. spectra were recorded on a Varian HR100 (100 MHz) spectrometer with tetramethylsilane as internal reference. Values are given with reference to the lines for HOD (τ 5.27) and Me_2CO (τ 7.84) in D_2O , and for Me_4Si in CDCl_3 . Mass spectra were run on an A.E.I. MS 902 instrument by the direct insertion method. The principal ion of an isotopic group is that containing ¹⁹³Ir and ³⁵Cl.

Hexachloroiridic acid, iridium tetrachloride, and iridium trichloride hydrate ($\text{IrCl}_3\cdot x\text{H}_2\text{O}$) were obtained from Johnson Matthey and used without further purification.

cis-Tetrachlorobis(dimethyl sulphoxide)iridic(III) Acid.—A solution of hexachloroiridic acid (1 g) in water (3 ml) and dimethyl sulphoxide (1.5 ml) was heated (reflux condenser) for 26 h on a boiling water bath; the colour changed from brown to yellow. The solution was evaporated to a small volume under vacuum and the residue was shaken with water and dichloromethane. The deep coloured aqueous layer was extracted with more solvent and then evaporated to a syrup under reduced pressure. Propan-2-ol (5 ml) and

dimethyl sulphoxide (0.5 ml) were added to the residue to give the *acid* (0.7 g) as yellow needles, m.p. 120–122° (Found: C, 15.3; H, 4.05; Cl, 21.6; S, 19.55. $\text{C}_6\text{H}_{13}\text{Cl}_4\text{IrO}_2\text{S}_2\cdot 2\text{Me}_2\text{SO}$ requires C, 14.85; H, 4.0; Cl, 21.9; S, 19.8%; ν_{max} , 1140s, 1100s, and 260m, 282m, 294m, and 325 cm^{-1} (Ir-Cl); τ (D_2O) 6.48 (s) and 7.31 (s) (1:1, the latter from the solvent of crystallisation).

Evaporation of the combined CH_2Cl_2 extracts and crystallisation of the residue from water gave a pale yellow *neutral complex* (0.12 g), m.p. 210–212° (Found: C, 13.5; H, 3.45; Cl, 19.9; S, 17.85%; M , 532. $\text{C}_6\text{H}_{18}\text{Cl}_3\text{IrO}_3\text{S}_3$ requires C, 13.55; H, 3.4; Cl, 19.95; S, 18.05%; M , 532); ν_{max} , 1140s (IrS=O), 925s (IrOS=O), and 232, 320, and 342 cm^{-1} (Ir-Cl); τ (CDCl_3) 6.34, 6.44, and 7.08 (1:1:1).

[This neutral complex was also obtained by heating a solution of iridium tetrachloride (1 g) in dimethyl sulphoxide (5 ml) on a steam-bath for 24 h under oxygen. The colour changed from purple to yellow. The solvent was removed under reduced pressure and the yellow residue was shaken with water (10 ml) and dichloromethane (3 × 10 ml); most of the colour passed into the organic layer. The aqueous layer was extracted with more solvent and the combined extract was dried (MgSO_4) and evaporated *in vacuo*. Acetone (2 ml) was added to the residue to give the complex (0.8 g); spectral characteristics as before.]

The *isoquinolinium salt* was made by dissolving the *cis*-acid (130 mg) in warm water (0.2 ml) and adding a solution of isoquinoline (50 mg) in ethanol (0.5 ml). The solution was cooled to 20° to give the salt (67 mg) as yellow plates, m.p. 186–191° (Found: C, 25.45; H, 3.3; Cl, 22.75; N, 2.95; S, 10.5. $\text{C}_{13}\text{H}_{18}\text{Cl}_4\text{IrNO}_2\text{S}_2$ requires C, 25.15; H, 3.25; Cl, 22.85; N, 2.25; S, 10.35%; ν_{max} , 260, 282, 294, and 325 cm^{-1} (Ir-Cl). The same procedure was used to prepare the *collidine salt*, yellow plates, m.p. 171–175° (Found: C, 23.65; H, 4.0; Cl, 23.35; N, 2.65; S, 10.6. $\text{C}_{12}\text{H}_{23}\text{Cl}_4\text{IrNO}_2\text{S}_2$ requires C, 23.5; H, 3.95; Cl, 23.15; N, 2.3; S, 10.45%), ν (Ir-Cl) as above.

trans-Tetrachlorobis(dimethyl sulphoxide)iridic(III) Acid.—A solution of chloroiridic acid (1 g) in propan-2-ol (10 ml) was kept at 55° for 3 h; the colour changed from red-brown to dark green. The mixture was then cooled to 15°. Addition of dimethyl sulphoxide (5 ml) caused the acid to begin to separate as pink *needles*. After 1 h the precipitate was collected and recrystallised from dimethyl sulphoxide-propan-2-ol (4:1); yield 1.3 g, m.p. 171.5–172° (Found: C, 14.8; H, 3.95; Cl, 21.9; S, 19.9%; ν_{max} , 1125s, 1010s, and 244w, 280m, 315s, and 335m cm^{-1} (Ir-Cl); τ (D_2O) 6.52 (s) and 7.31 (s) (1:1, latter from solvate Me_2SO).

The acid (130 mg) was converted by the method for the *cis*-acid into its *isoquinoline salt* (32 mg), tan needles, m.p. 165–170° (Found: C, 25.05; H, 3.2; Cl, 23.0; N, 2.45; S, 10.3%; ν_{max} , 244, 280, 315, and 335 cm^{-1} (Ir-Cl); and its *collidine salt*, fawn needles, m.p. 171–174° (Found: C, 23.45; H, 3.7; Cl, 23.4; N, 2.5; S, 10.65%; ν (Ir-Cl) as above.

The *cis*-acid is converted into the *trans*-acid to a considerable extent either when kept in the solid state at room temperature for 2–3 months or when heated in methanol solution for 24 h. When the *trans*-acid was kept in aqueous dimethyl sulphoxide at *ca.* 90° it was appreciably converted into the more polar *cis*-acid.

trans-Dichloro-mer-tris(dimethyl sulphoxide)hydrido-iridium (I).—The *trans*-acid (0.5 g, 1 mol) was dissolved in

⁷ L. Vaska, *J. Amer. Chem. Soc.*, 1961, **83**, 756; L. Vaska and J. W. Diluzio, *ibid.*, 1962, **84**, 4989.

water (0.5 ml) and propan-2-ol (15 ml) and dimethyl sulphoxide (0.06 g, 1 mol) were added. The mixture was heated at 55° (thermostatic control) for 24 h under nitrogen, the colour changing from orange to yellow. The solution was then left at room temperature under nitrogen for 24 h; yellow crystals separated. The product was washed with propan-2-ol-di-isopropyl ether to afford the hydride (0.136 g, 37%), m.p. 184—185°. Crystallisation from dimethyl sulphoxide (1 ml)—propan-2-ol (0.3 ml) and *n*-hydrochloric acid (0.2 ml) gave yellow prisms, m.p. 184.5—185° (Found: C, 14.6; H, 3.95; Cl, 14.05; S, 19.1. $C_8H_{10}Cl_2IrO_3S_3$ requires C, 14.45; H, 3.85; Cl, 14.25; S, 19.3%; ν_{max} , 2190 and 833 (Ir-H), 1120s and 1015s (S=O), and 334s and 300w cm^{-1} (Ir-Cl); τ (CDCl₃) 35.29 (s). The mother liquor was kept at 0° for 2 days to give more hydride (0.13 g), m.p. 182—184°.

The hydride (20 mg) was also obtained by keeping a solution of the *trans*-acid (50 mg) in water (0.05 ml) and propan-2-ol (2 ml) at 15° for 7 days.

A solution of the *trans*-acid (0.1 g) in propan-2-ol (5 ml) and water (0.05 ml) was kept at 82° for 6 h in a sealed ampoule. The solvent was distilled off and the distillate was treated with 2,4-dinitrophenylhydrazine sulphate reagent. Purification *via* chromatography gave acetone 2,4-dinitrophenylhydrazone (23 mg, 63%).

cis-Dichloro-mer-tris(dimethyl sulphoxide)iridium (IIa).—The *cis*-acid (0.25 g) was dissolved in water (0.25 ml) and propan-2-ol (7 ml) and dimethyl sulphoxide (0.03 g) were added. The mixture was heated at 60° for 24 h, then cooled to 20°, and a small quantity of di-isopropyl ether was added. After 24 h at room temperature yellow crystals of the hydride (60 mg) had separated; m.p. 160—165° (Found: C, 14.5; H, 3.45; Cl, 14.65; S, 19.6%); ν_{max} , 2180 and 813 (Ir-H), 1130s and 1030s (S=O), and 335s, 312m, and 282m cm^{-1} (Ir-Cl); τ (CDCl₃) 28.84 (s). This hydride is unstable in solution and in the solid state. After 2 days at 0° some hydride (I) (90 mg) had separated from the mother liquor.

The hydride (IIa) (8 mg) was also obtained by keeping a solution of the *cis*-acid (50 mg) in water (0.05 ml) and propan-2-ol (2 ml) at 15° for 7 days.

A solution of the neutral complex, $IrCl_3(Me_2SO)_3$ (0.1 g) in propan-2-ol (3 ml) and water (0.1 ml) was heated at 90° for 3 h. Evaporation under reduced pressure gave a residue containing the hydrides (I) and (IIa) in *ca.* 7:3 ratio (estimation by i.r.).

Trichlorotris(dimethyl sulphoxide)iridium (III).—(a) A solution of iridium tetrachloride (2 g) in dimethyl sulphoxide (6 ml) and cyclopentanol (3 ml) was heated at 90° for 24 h under oxygen; the colour changed from purple to dark brown. Addition of propan-2-ol (10 ml) to the cooled mixture caused a brown solid to separate. This, in benzene, was placed on neutral alumina (100 g), and the column was eluted with benzene (3 × 100 ml). The third fraction gave a solid mixture (0.6 g), which was treated with methanol, in which the complex $IrCl_3(Me_2SO)_3$ with one group *O*-bonded, is fairly soluble. The remaining less soluble cream complex (III) (0.15 g) had m.p. 171—172° (Found: C, 14.2; H, 3.75; Cl, 19.75; S, 18.05%; *M*, 532); ν_{max} , 1150s, 1025m, and 332s, 306s, and 278w cm^{-1} (Ir-Cl); τ (CDCl₃) 6.46 (s) and 6.55 (s) (1:2).

(b) The hydride (I) (50 mg) dissolved in chloroform (2 ml) was added to a mixture of potassium permanganate (0.1 g) in a small quantity of water and 5*N*-hydrochloric acid (1 ml). The mixture was gently shaken at room temperature for a few minutes. The chloroform layer was dried (MgSO₄) and evaporated to give a yellow solid. Crystallisation from methanol afforded the complex (40 mg) (i.r. identification).

(c) The hydride (I) (0.1 g) was dissolved with gentle warming in ethanol (2 ml) and *n*-hydrochloric acid (0.5 ml); gas was evolved. The solvent was evaporated off and the product was separated with dichloromethane and water. The organic extract gave the complex (50 mg) (i.r. identification). Evaporation of the aqueous phase gave the *trans*-acid (40 mg).

When a solution of this complex (III) (50 mg) was kept at 15° for 2 days, the hydride (IIa) (30 mg) separated as a pale yellow solid, m.p. 162—165° (i.r. identification).

Chlorotris(dimethyl sulphoxide)dihydridoiridium (IV).—

(a) The hydride (I) (0.1 g, 1 mol) was dissolved in warm propan-2-ol (10 ml) and water (1 ml) and then dimethyl sulphoxide (0.042 g, 3 mol) were added. The yellow mixture was heated on a steam-bath for 20 h; it had then become colourless. Evaporation under reduced pressure to a small volume afforded white needles which were washed with propan-2-ol-di-isopropyl ether (2:1) to yield the dihydride (60 mg) as white needles, m.p. 164—165° (Found: C, 15.85; H, 4.05; Cl, 8.35; S, 20.35. $C_8H_{20}ClIrO_3S_3$ requires C, 15.55; H, 4.75; Cl, 7.65; S, 20.75%); ν_{max} , 2170 and 2250 (Ir-H), 830, and 854 cm^{-1} ; τ (CDCl₃) 29.5 (d) and 26.3 (d) (*J* 5.85 Hz), and 7.22, 6.48, and 6.44 (each s, Me, 1:1:1).

(b) A yellow solution of the complex $IrCl_3(Me_2SO)_3$ containing one *O*-bonded ligand (0.2 g) and dimethyl sulphoxide (0.06 g) in propan-2-ol (9 ml) and water (1 ml) was heated at 68° for 24 h; it was then colourless. The solution was evaporated to a small volume. After 24 h at room temperature the dihydride (80 mg) crystallised as prisms, m.p. 164—165° (i.r. identification).

Deuteriodichlorotris(dimethyl sulphoxide)iridium.—(a) The hydride (I) (0.1 g) was added to a solution of dimethyl sulphoxide (0.2 ml), *n*-deuterium chloride (0.2 ml), and propan-2-[²H]ol (0.3 ml), and the mixture was heated at 70° for 1 h under nitrogen. On cooling the deuteride (80 mg) separated as yellow crystals, m.p. 184—185°; ν_{max} , 1560 and 833 cm^{-1} (Ir-D).

(b) The *trans*-acid (0.08 g) was dissolved in the same mixture of solvents and heated at 50° under nitrogen for 24 h. The colour changed from orange to yellow. The mixture was kept at 0° for 24 h. The yellow deuteride (0.04 g), m.p. 183—185°; ν_{max} , 1560 and 833 cm^{-1} (Ir-D), had then separated.

When the *trans*-acid (0.1 g) was heated under reflux with [²-²H]propan-2-ol (2.5 ml) for 18 h the product, obtained by evaporation, showed i.r. absorption at 2170 and not at 1560 cm^{-1} .

We thank Glaxo Research and Queen's University for financial assistance (to Y. M. Y. H. and J. T-G., respectively).

[2/2474 Received, 1st November, 1972]