

Hyrido Complexes of Iridium with a Tertiary Arsine

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Summary

Two isomeric series (α and β) of hydrido complexes of iridium with methyldiphenyl arsine of the general formula $\text{IrHX}_2(\text{Ph}_2\text{AsMe})_3$ ($\text{X} = \text{Cl, Br or I}$) have been prepared and characterised. The α compounds are prepared by reacting the metal halide and the arsine in alcoholic medium with zinc and the corresponding halogen acid, while the β compounds are prepared by refluxing the metal halide and the arsine in alcoholic medium in presence of potassium hydroxide. The properties of these hydrido complexes are compared with the corresponding trihalogeno complexes of the general formula $\text{IrX}_3(\text{Ph}_2\text{AsMe})_3$. Hydrides of rhodium of the general formula $\text{RhHX}_2(\text{Ph}_2\text{AsMe})_3$, prepared earlier using hypophosphorous acid as reducing agent, can be made by other methods.

Inhaltsübersicht

Es wurden zwei isomere (α - und β -) Reihen von Hydridokomplexen des Iridiums mit Methyldiphenylarsin, $\text{IrHX}_2(\text{Ph}_2\text{AsMe})_3$ ($\text{X} = \text{Cl, Br oder I}$), dargestellt und untersucht. Zum Vergleich wurden auch die entsprechenden Trihalogenokomplexe $\text{IrX}_3(\text{Ph}_2\text{AsMe})_3$ dargestellt. Hydridokomplexe des Rhodiums, $\text{RhHX}_2(\text{Ph}_2\text{AsMe})_3$, wurden nach einer neuen Methode erhalten.

Introduction

The hydrido compound of iridium $\text{IrHBr}_2(\text{Ph}_2\text{AsMe})_3$ has been prepared earlier by reacting iridium bromide in alcoholic solution with the arsine in presence of the corresponding halogen acid and hypophosphorous acid¹⁾. Attempts to prepare the hydridochloride and -iodide by the above method were not successful. Hence several other methods were tried to obtain these compounds. These attempts have yielded two isomeric series (α and β) of the three hydridohalides.

Experimental Results and Discussion

The isomeric series of hydrido compounds of iridium may be prepared by two different methods. The α compounds have been prepared by treating

¹⁾ J. LEWIS, R. S. NYHOLM and G. K. N. REDDY, Chem. and Ind. 1960, 1386.

the iridium halide in alcoholic solution with zinc dust and the corresponding halogen acid in presence of a calculated quantity of methyldiphenyl arsine²).

It may be pointed out here that though zinc has been used earlier in the preparation of compounds containing metal-hydrogen bonds³⁻⁵), this is perhaps the first instance wherein it is used with a halogen acid to prepare transition metal hydride complexes stabilised by a tertiary arsine. Cadmium can also be used in place of zinc; however, the reaction is much slower with the former.

The β compounds are obtained by CHATT's method⁶) which consists in boiling the metal halide with the arsine in alcoholic medium in presence of calculated amount of potassium hydroxide. (The β form of the iodo compound, however, could not be obtained in a pure form). Prolonged boiling, however, converts the β compounds into the α compounds suggesting that the α form is the more stable one.

The α compounds (Table 1) are lighter in their colour and show metal-hydrogen stretching modes in the 2200 cm^{-1} region while the β compounds are brighter in their colour and show metal-hydrogen stretching modes in the 2100 cm^{-1} region in the infrared. These hydrido complexes are non-electrolytes in nitrobenzene and reduce alcoholic silver nitrate to metallic silver.

Table 1
Characterisation of Compounds

Compound	colour	M. P. in °C	Infrared bands, cm^{-1}	
			stretching	bending
$\text{IrCl}_3(\text{Ph}_2\text{AsMe})_3$	Yellow	138-140		
$\text{IrBr}_3(\text{Ph}_2\text{AsMe})_3$	Orange	223-226		
$\text{IrI}_3(\text{Ph}_2\text{AsMe})_3$	Orange-Brown	227-228		
$\text{IrHCl}_2(\text{Ph}_2\text{AsMe})_3$ (α)	white	225-227	2210	800
$\text{IrHCl}_2(\text{Ph}_2\text{AsMe})_3$ (β)	Yellow	217-219	2095	800
$\text{IrHBr}_2(\text{Ph}_2\text{AsMe})_3$ (α)	Pale yellow	228-231	2210	780
$\text{IrHBr}_2(\text{Ph}_2\text{AsMe})_3$ (β)	Orange	237-239	2095	795
$\text{IrHI}_2(\text{Ph}_2\text{AsMe})_3$ (α)	Pale orange	236-239	2195	-
$\text{IrHI}_2(\text{Ph}_2\text{AsMe})_3$ (β)	Orange-red	217-221 (impure)	2095	780
$\text{RhHCl}_2(\text{Ph}_2\text{AsMe})_3$	Yellowish-orange	157-159	2090	-
$\text{RhHBr}_2(\text{Ph}_2\text{AsMe})_3$	Orange	160-165	2090	-
$\text{RhHI}_2(\text{Ph}_2\text{AsMe})_3$	Brown	150-154	2075	-

²) G. K. N. REDDY and E. G. LEELAMANI, Proc. Indian. Science Congress 1967, part III, Sec. IV, p. 113.

³) G. E. F. LUNDELL and H. B. KNOWLES, J. Res. nat. Bur. Standards 18, 629 (1937); A. P. GINSBERG, J. M. MILLER and E. KOUBEK, J. Amer. chem. Soc. 83, 4909 (1961); A. P. GINSBERG and E. KOUBEK, Z. anorg. allg. Chem. 315, 278 (1962).

⁴) E. L. SMITH and L. MERVYN, Biochem. J. 86, 2 (1963); S. L. TACKETT, J. W. COLLAT and J. C. ABBOTT, Biochem. 2, 919 (1963); J. chem. Soc. [London] 1963, 414.

⁵) J. A. OSBORN, A. R. POWELL and G. WILKINSON, Chem. Commun. 1966, 461.

⁶) J. CHATT and B. L. SHAW, Chem. and Ind. 1960, 931; 1961, 290.

Corresponding trihalogeno compounds of the general formula $\text{IrX}_3(\text{Ph}_2\text{AsMe})_3$ have also been prepared with a view to compare their properties with those of the hydrido complexes.

These trihalogeno compounds are obtained by refluxing the metal halide and the calculated amount of the arsine in methoxyethanol. (These compounds have been prepared earlier by a slightly different method by DWYER and NYHOLM⁷⁾). They are more intensely coloured than the hydrides, are more easily soluble in nonpolar organic solvents and are non-electrolytes in nitrobenzene.

Some of the properties of the trihalogeno compounds and the hydrides are tabulated in table 1.

It is seen that in the zinc and halogen acid reduction method as well as in the base-catalyzed reduction process an alcoholic medium is used. It has been reported earlier that alcohol tends to produce hydride complexes when it is used as a solvent for the reaction between iridium bromide and tertiary arsines⁸⁾. So in order to have a clarification on this point, the above experiments of preparing the hydrido complexes were repeated in alcoholic medium without using either zinc and halogen acid or potassium hydroxide.

Thus a mixture of potassium chloroiridate(III) and the arsine was refluxed in ethyl alcohol for 30 hours. The solid product obtained consisted of a large amount of the trichloro compound $\text{IrCl}_3(\text{Ph}_2\text{AsMe})_3$ and a small amount of both the α and β forms of the hydride $\text{IrHCl}_2(\text{Ph}_2\text{AsMe})_3$ as shown by the infrared spectrum and elemental analysis. A similar treatment for 30 hours of ammonium bromoiridate(III), however, gave a pure sample of the α form of the hydridobromide, while only a very small amount of the α form of the hydriodide could be made this way.

It may be noted that these results in pure alcoholic medium were obtained only after the reaction was carried out for 30 hours while when zinc and halogen acid or potassium hydroxide are used the maximum time required for the completion of the reaction to produce the hydride is two hours, very often it is even much less.

On an analogy with similar compounds of iridium⁹⁾ and rhodium¹⁰⁾ reported in the literature, we assign an octahedral configuration for the two series of iridium compounds prepared, the hydrogen occupying a position trans to the halogen of weaker trans-effect in the α compounds, and trans to the arsine of stronger trans-effect in the β compounds.

Hydrido compounds of rhodium of the general formula $\text{RhHX}_2(\text{Ph}_2\text{AsMe})_3$ where $\text{X} = \text{Cl, Br or I}$ have been prepared earlier by using hypophosphorous acid as a reducing agent¹⁾. It is now found that these compounds may be prepared both by the zinc and halogen acid reduction method²⁾ as well as by CHATT's method of reduction with alcoholic potash⁶⁾

⁷⁾ F. P. DWYER and R. S. NYHOLM, J. Proc. Roy. Soc. New South Wales **79**, 121 (1945).

⁸⁾ J. CHATT, A. E. FIELD and B. L. SHAW, J. chem. Soc. [London] **1963**, 3371.

⁹⁾ J. CHATT, R. S. COFFEY and B. L. SHAW, J. chem. Soc. [London] **1965**, 7391.

¹⁰⁾ A. SACCO, R. UGO and A. MOLES, J. chem. Soc. [London] Sect. A **1966**, 1670.

used for the iridium hydrides. Their identity is established by analysis and by their infrared spectra. It is further found that all the three methods give rise to only one series of compounds. Attempts to prepare the two α and β series as in the case of iridium were not successful.

Experimental

Infrared spectra were taken in Nujol mulls using a Carl Zeiss UR 10 Spectrophotometer. Microanalysis on the samples were carried out at the MAX-PLANCK-Institute, West Germany and CIBA Research Laboratories, Bombay.

Hydridodichloro-tris-(methyldiphenylarsine)-iridium(III) (α form). 0.28 gram of $\text{Na}_3\text{IrCl}_6 \cdot 12 \text{H}_2\text{O}$ (0.4 millimole) in 2 ml of water and 4 ml of concentrated hydrochloric acid was treated with 0.3 gm of methyl diphenyl arsine (1.2 millimole) in 20 ml of alcohol. Zinc dust was added in small quantities when the hydrido compound got separated as shining very pale yellow crystals. The contents were refluxed for two hours with intermittent addition of zinc and acid. The solution was filtered off and the hydrido compound was recrystallised from chloroform-petroleum ether and dried in vacuum. Yield 200 mg ($\text{C}_{39}\text{H}_{40}\text{Cl}_2\text{As}_3\text{Ir}$ requires C 47.0, H 4.0, Cl 7.1%; found: C 46.8, H 4.0, Cl 6.9%).

Hydridodibromo-tris-(methyldiphenylarsine)-iridium(III) (α form). Prepared similar to the chloro compound using freshly distilled 30% hydrobromic acid in place of hydrochloric acid. Yield: 0.27 gm ($\text{C}_{39}\text{H}_{40}\text{Br}_2\text{As}_3\text{Ir}$ requires C 43.1, H 3.7 and Br 14.7%; found: C 43.1, H 4.0, Br 15.4%).

This compound was also prepared using cadmium for reduction instead of zinc. The reduction was carried out for 6 hours. Yield 0.2 gm. (found C 43.31, H 3.96%).

The bromo compound was also obtained by refluxing for 30 hours ammonium bromo-iridate and the arsine in alcohol in the absence of hydrobromic acid and zinc (found: C 43.05, H 3.41%).

Hydridodiiodo-tris-(methyldiphenylarsine)-iridium(III) (α form). Prepared similar to the chloro and bromo compounds using freshly distilled hydriodic acid. Yield: 0.31 gm ($\text{C}_{39}\text{H}_{40}\text{I}_2\text{As}_3\text{Ir}$ requires C 39.72, H 3.42, I 21.52%; found: C 39.66, H 3.36, I 21.45%).

Hydridodichloro-tris-(methyldiphenylarsine)-iridium(III) (β form). 0.2 gm of K_3IrCl_6 (0.4 millimole) was dissolved in 2 ml of water and 0.30 gm (1.2 millimole) of methyl diphenyl arsine in 20 ml of alcohol was added followed by 4 ml of 0.1 N potassium hydroxide (0.4 millimole). The mixture was refluxed for two hours, cooled, filtered and the hydrido compound was washed first with alcohol and then several times with water followed again with alcohol and dried in vacuum. Yield: 0.17 gm ($\text{C}_{39}\text{H}_{40}\text{Cl}_2\text{As}_3\text{Ir}$ requires C 47.0, H 4.05, and Cl 7.1%; found: C 46.8, H 4.00 and Cl 6.94%).

Hydridodibromo-tris-(methyldiphenylarsine)-iridium(III) (β form). Prepared similar to the chloro compound starting with 0.28 gm ammonium bromo-iridate(III). Yield: 0.25 gm ($\text{C}_{39}\text{H}_{40}\text{Br}_2\text{As}_3\text{Ir}$ requires C 43.1, H 3.7, Br 14.7, As 20.70%; found: C 43.05, H 3.78, Br 14.95, As 20.90%).

Hydridodiiodo-tris-(methyldiphenylarsine)-iridium(III) (β form). 0.2 gm of K_3IrCl_6 (0.4 millimole) was dissolved in 2 ml of water. 0.3 gm (1.2 millimoles) of methyldiphenyl arsine in 25 ml alcohol was added followed by 4 ml of 0.1 N (0.4 millimole) potassium hydroxide. The mixture was refluxed for few minutes and 1 gm of sodium iodide in 3 ml of hot water was added and the refluxing continued for 2 hours. The hydrido compound was separated as usual and identified by its infrared spectrum. The compound has not been obtained in a pure form.

Trichloro-tris-(methyldiphenylarsine)-iridium(III). 0.1 gm (0.2 millimole) of K_3IrCl_6 was dissolved in 2 ml of water. 4 ml of concentrated hydrochloric acid was added followed by 0.16 gm (0.65 millimole) of methyldiphenyl arsine in 10 ml of methoxyethanol. The mixture was refluxed for 20 minutes and water was added till the solution was turbid. The refluxing was continued for another 15 minutes when yellow crystals got separated. Yield: 0.14 gm ($C_{39}H_{39}Cl_3As_3Ir$ requires C 45.43, H 3.82%; found: C 45.64, H 4.14%).

Tribromo-tris-(methyldiphenylarsine)-iridium(III). Prepared as above using freshly distilled hydrobromic acid in place of hydrochloric acid. Yield: 0.18 gm ($C_{39}H_{39}Br_3As_3Ir$ requires C 40.27, H 3.38%; found C 40.64, H 3.78%).

Triiodo-tris-(methyldiphenylarsine)-iridium(III). Prepared as above using freshly distilled hydriodic acid. Yield: 0.4 gm. ($C_{39}H_{39}I_3As_3Ir$ requires C 35.9, H 3.0%; found: C 35.99, H 3.33%).

Hydridodichloro-tris-(methyldiphenylarsine)-rhodium(III). 0.26 gm (1 millimole) of $RhCl_3 \cdot 3 H_2O$ was dissolved in 2 ml of water and 4 ml of concentrated hydrochloric acid was added followed by 0.75 gm (3 millimoles) of methyl diphenyl arsine in 25 ml alcohol. The mixture was refluxed with the intermittent addition of zinc dust for 4 hours. The hydrido compound was recrystallised from chloroform-petroleum ether mixture. Yield: 0.32 gm ($C_{39}H_{40}Cl_2As_3Rh$ requires C 51.6, H 4.4, Cl 7.8, As 24.8%; found: C 51.6, H 4.22, Cl 8.01, As 24.74%).

The compound was also prepared using 10 ml of 0.1 N potassium hydroxide (1 millimole) in place of zinc and hydrochloric acid. Yield: 0.30 gm (found: C 51.75, H 4.66%).

Hydridodibromo-tris-(methyldiphenylarsine)-rhodium(III). Prepared as in the case of the hydrido chloride using 0.35 gm of rhodium bromide and zinc and freshly distilled hydrobromic acid. Yield: 0.35 gm ($C_{39}H_{40}Br_2As_3Rh$ requires C 47.0, H 4.0%; found: C 46.44 and H 4.0%).

Hydridodiiodo-tris-(methyldiphenylarsine)-rhodium(III). Prepared as in the case of the hydrido chloride using 0.26 gm of $RhCl_3 \cdot 3 H_2O$ and freshly distilled hydriodic acid. Yield: 0.4 gm ($C_{39}H_{40}I_2As_3Rh$ requires C 43.0, H 3.7; As 20.6%; found: C 42.63, H 3.89; As 20.39%).

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