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FINAL REPORT

NEW HYDRIDES OF TRANSITION METALS

by

prof. LAMBERTO MALATESTA

INSTITUTE OF GENERAL CHEMISTRY

UNIVERSITY of MILANO (Italy)

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AF EOAR GRANT 62-34

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## FINAL TECHNICAL REPORT

November 1st, 1961

October 31st, 1963

## GENERAL SUMMARY

The researches carried out with Grant 62-34 is giving origin to five different papers, here reported as Parts I - V and to some very interesting preliminary results reported as Part VI.

Part I - "HYDRIDOCOMPLEXES OF RHODIUM(I) AND OF COBALT(I)

by A. Sacco and R. Ugo, which has been published as Technical Report N. 1, has been accepted for the publication on the "Journal of the Chemical Society". In it the preparation and the properties of the new cobalt and rhodium hydrides with 1,2-bis(diphenylphosphino)ethane (DPE) of formula  $\text{CoH}(\text{DPE})_2$  and  $\text{RhH}(\text{DPE})_2$  are described.

Part II - "HYDRYDOTRIPHENYLPHOSPHINERHENIUM COMPOUNDS"

by L. Malatesta, M. Freni and V. Valenti, will be published in a scientific journal in the next future. In it are described the preparation and properties of two unusual and interesting complex rhenium hydrides, one of which fully characterized i.e.  $\text{ReH}_5[\text{P}(\text{C}_6\text{H}_5)_3]_3$ , the other  $\text{Re}_{5-7}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  still uncertain, as for the number of hydridic hydrogen.

Part III - "TRIHYDRIDOTRIPHENYLPHOSPHINEIRIDIUM COMPOUNDS"

by M. Angoletta, has been published in "Gazzetta Chimica Italiana" vol. 92, 811, (1962). In it the preparation of the trihydridotris-

(triphenylphosphine)iridium and the isolation of the two isomeric cis and trans forms of this hydride are described.

Part IV - "SUBSTITUTION DERIVATIVES OF TRIHYDRIDOTRIS(TRIPHENYL-PHOSPHINE)IRIDIUM" - by M. Angoletta and A. Araneo, which will be published in "Gazzetta Chimica Italiana" vol. 93, (1963). In it the derivatives of the reaction of trihydrido(triphenylphosphine)iridium with halogen acids, halogens, oxo and organic acids are described, and the reaction of dihydridotris(triphenylphosphine)<sup>iridium</sup> perchlorate with neutral and anionic ligands are studied.

Part V - "NEW HYDRIDO-AND HYDRIDOCARBONYL-TRIPHENYLPHOSPHINE-IRIDIUM COMPOUNDS" - by L. Malatesta, M. Angoletta and G. Caglio. This work has been accepted by, and will be presented at, "The International Conference on Coordination Chemistry (VIII ICC) to be held in Vienna on September 1964. In it the preparation and complex relationships of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ ;  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ ;  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ ;  $\text{IrH}_3\text{CO}[\text{P}(\text{C}_6\text{H}_5)_2]_2$  and their derivatives are described.

Part VI - gives the preliminary results obtained by Malatesta, Naldini and others during attempts to prepare complex hydrides of the coinage metals. This research will be carried to end with Grant AF EOAR 64/9.

Part I." HYDRIDOCOMPLEXES OF RHODIUM(I) AND OF COBALT(I) "

by A. Sacco and R. Ugo

Summary. The preparation and properties of complex salts of rhodium(I), of formula  $[\text{Rh}(\text{C}_2\text{H}_4\{\text{PPh}_2\}_2)_2]\text{X}$  ( $\text{X} = \text{Cl}, \text{ClO}_4, \text{BPh}_4$ ), are described. From these a stable hydrido-complex of rhodium(I), of formula  $[\text{RhH}(\text{C}_2\text{H}_4\{\text{PPh}_2\}_2)_2]$  is prepared by reduction with lithium aluminium hydride and with sodium borohydride. The product of reaction between  $\text{CoBr}_2(\text{C}_2\text{H}_4\{\text{PPh}_2\}_2)_2$  and sodium borohydride, previously described as a derivative of cobalt(0), is shown to be a hydrido-complex of cobalt(I), of formula  $[\text{CoH}(\text{C}_2\text{H}_4\{\text{PPh}_2\}_2)_2]$ . This formula is proved by the diamagnetism of the compound, by its infrared spectrum and by its reaction with carbon tetrachloride to give chloroform. The dipole moments, of the order of 3 - 4 D, suggest a non-ortogonal structure for these hydrido-complexes of rhodium and cobalt.

A number of stable hydrido-complexes of transition-metals, of general formula  $[MH_xL_z]$ , where X is an anionic ligand and L is a tertiary phosphine or arsine, have been prepared in these last years.<sup>(1)</sup> Among the metals of the cobalt group, many very stable derivatives of iridium<sup>(2)</sup> and only a few of rhodium<sup>(3)</sup> are known. The only hydrido-complex of cobalt, stabilised by a tertiary phosphine, is the compound  $[CoH(C_2H_4\{PPh_2\}_2)_2]$ , which has been recently prepared (together with the corresponding deuteride) in these laboratories<sup>(4)</sup> by reduction of  $[CoBr_2(C_2H_4\{PPh_2\}_2)_2]$  with lithium aluminium hydride (and deuteride resp.) in tetrahydrofuran.

In this paper we describe the preparation and properties of some complex salts of rhodium(I) of formula  $[Rh(DPE)_2]X$  (DPE = 1,2-bis(di-phenylphosphino)ethane; X = Cl, ClO<sub>4</sub>, BPh<sub>4</sub>), the preparation and properties of a new very stable hydrido-complex of rhodium(I), of formula  $[RhH(DPE)_2]$ , and we prove that the product of the reaction between  $CoBr_2(DPE)_2$  and sodium borohydride, previously described<sup>(5)</sup> as a derivative of cobalt(0), actually is a hydrido-complex of cobalt(I), of formula  $[CoH(DPE)_2]$ .

The compound  $[Rh(DPE)_2]Cl$  is easily prepared from  $[Rh(CO)_2Cl]_2$  and the diphosphine in benzene. It is a stable, yellow, crystalline substance, soluble in polar organic solvents, in which it is ionised, insoluble in hydrocarbons. The corresponding perchlorate and tetraphenylborate are readily obtained by exchange in alcoholic solution.

Preparation of Hydrido-complexes. The hydrido-complex of rhodium(I) is obtained by reduction of  $[\text{Rh}(\text{DPE})_2]\text{Cl}$  with lithium aluminium hydride in tetrahydrofuran or with sodium borohydride in ethanol. It is an orange, crystalline compound, rather soluble in benzene, insoluble in alcohols and light petroleum. It shows a considerable thermal stability (m.p.  $240^\circ$ ; decomp.  $280^\circ$ ), but it is rapidly oxidised by air.

The deuteride is obtained in a similar way with lithium aluminium deuteride in tetrahydrofuran, and it can be recrystallized by adding ethanol to its benzene solution without undergoing any detectable exchange.

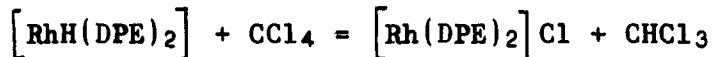
The hydrido-complex of cobalt(I), prepared by reduction of  $\text{CoBr}_2(\text{DPE})_2$  with sodium borohydride either in absolute or in aqueous ethanol, is exactly alike, both before and after recrystallisation from benzene-ethanol and from dimethylformamide, to the compound obtained by reduction with lithium aluminium hydride <sup>(4)</sup>.

Infrared Absorption Spectra. The infrared spectrum of the hydrido-complex of rhodium(I) shows a strong sharp band at  $1902\text{ cm}^{-1}$ , due to the metal-hydrogen stretching vibration; the spectrum of the corresponding deuterido-derivative shows a sharp strong band at  $1465\text{ cm}^{-1}$  (ratio of hydride to deuteride stretching frequencies equal to 1.39). Moreover, the spectrum of the hydrido-complex shows a band at  $626\text{ cm}^{-1}$  which does not appear in the spectrum of the deuterido-complex, and which we tentatively assign to the bending mode  $\delta$  (Rh-H).

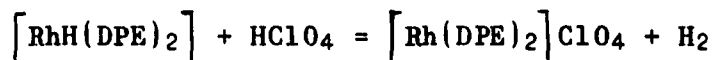
The infrared spectrum of the hydrido-complex of cobalt(I) shows a band of medium intensity at  $1884\text{ cm}^{-1}$ , ascribable, by comparison with the spectrum of the corresponding deuteride <sup>(4)</sup>, to the stretching mode  $\nu(\text{Co-H})$ .

The increase in M-H stretching frequencies, found going from cobalt to rhodium, is in agreement with the increase of M-H bond strength generally observed in passing from the light to the heavy elements.

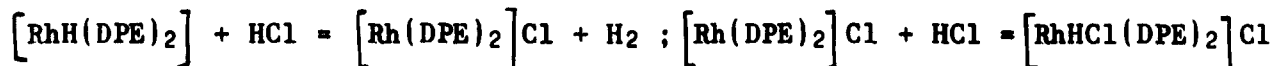
Reactions. The hydrido-complex of rhodium(I) reacts at room temperature with carbon tetrachloride according to:



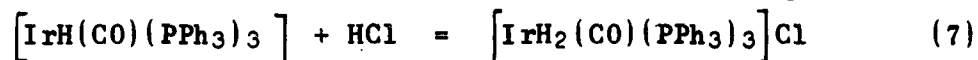
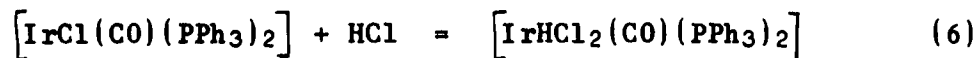
and with perchloric acid, in aqueous ethanol, giving off hydrogen according to the equation:



By treating the hydride with hydrogen chloride in the same conditions, it still reacts giving off hydrogen in a molar ratio hydrogen to complex of 1 to 1, but the product of the reaction contains two atoms of chlorine per atom of rhodium and behaves as a uni-univalent electrolyte. This compound is diamagnetic and shows in the infrared spectrum a weak band in the region of the metal-hydrogen stretching vibrations, i.e. at  $2110\text{ cm}^{-1}$ . The same compound is also obtained by treating  $[\text{Rh}(\text{DPE})_2]\text{Cl}$  with hydrogen chloride in ethanol under nitrogen, and therefore we consider it as a hydrido-complex of trivalent rhodium, formed as follows:



Though further studies will be undertaken to prove this formulation, this is supported by the analogous addition of hydrogen chloride to the iridium(I) complexes, according to:



and to the platinum(II) complex <sup>(8)</sup> of formula  $[\text{PtHCl}(\text{PEt}_3)_2]$  to give  $[\text{PtH}_2\text{Cl}_2(\text{PEt}_3)_2]$ .

The hydrido-complex of cobalt(I) does not give off hydrogen by action of hydrogen chloride or perchloric acid, though it reacts giving products still under study. With carbon tetrachloride it gives chloroform and not yet identified cobalt derivatives.

Dipole moments and structure. The hydrido-complex of rhodium(I) in benzene solution has a moment of 4.35 D, assuming  $P_A = 0$ , or 4.03 D, assuming  $P_A = 0.20 P_E$ . The hydrido-complex of cobalt(I) has a moment of 3.50 D ( $P_A = 0$ ) or 3.08 D ( $P_A = 0.20 P_E$ ).

The values of the dipole moments (4.2 - 4.9 D) determined by Chatt <sup>(1)</sup> for the hydrido complexes of the type trans- $[\text{PtHCl}(\text{PR}_3)_2]$  and trans- $[\text{MHCl}(\text{C}_2\text{H}_4\{\text{PEt}_2\}_2)_2]$  (in which M = Fe, Ru, Os) indicate that the metal-hydrogen bond moment is certainly less than 2 D, <sup>may</sup>owing to the increased negative character of the trans-halogen under the influence of the hydride ligand, probably much less than 2 D. Therefore, we can exclude for the hydrido-complexes of rhodium(I) and cobalt(I) a tetragonal structure with the four phosphorus atoms on the same plane of

the metal. The values of the dipole moments of these hydrido-complexes rather suggest a distorted tetrahedral arrangement of the phosphorus atoms surrounding the central metal atom, with the hydrogen atom situated along a trigonal axis. This type of structure, similar to that proposed for the cobalt tetracarbonyl hydride <sup>(9)</sup>, would account for the asserted isomorphism of Chatt's compound <sup>(5)</sup>, now shown to be a hydrido-derivative, with the tetracoordinated complexes of nickel(0) and palladium(0) with the same diphosphine.

The compounds here described represent the first example of very stable hydrido-complexes with a non-orthogonal configuration and with the metal in the oxidation state +1.

Nuclear Magnetic Resonance. The spectra of the hydrido-complexes, carried out in deuterated benzene with the Varian 4310 C apparatus, did not show any band assignable to the proton resonance of the hydridic hydrogen, probably for one or more of the following reasons: poor solubility of the compounds in benzene; inadequate sensitivity of the apparatus; splitting of the hydrogen band in a number of very weak bands, owing to the interaction of the proton with the phosphorus nuclei of spin 1/2. The very sharp bands shown by the C<sub>6</sub>H<sub>5</sub> and CH<sub>2</sub> groups of the ligand confirm the diamagnetism of these compounds, independently determined by Gouy's method for the solid state.

EXPERIMENTAL

The diphosphine  $(\text{CH}_2.\text{PPh}_2)_2$  was prepared as described by Chatt and Hart (10). The hydrido-complexes were manipulated in an atmosphere of dry nitrogen, and their m.p.s. were determined in evacuated tubes. The infrared spectra were obtained in Nujol with the Perkin-Elmer 237 spectrometer.

Di- $\{1,2\text{-bis(diphenylphosphino)ethane}\}$ rhodium(I) chloride.

$[\text{Rh}(\text{C}_2\text{H}_4\{\text{PPh}_2\}_2)_2]\text{Cl}$ . A solution of the diphosphine (3.1 g, 2 mols) in benzene (20 cc) was added to a solution of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (0.7 g, 1 mol) in benzene. The resulting yellow precipitate was collected, washed with warm benzene and dried. The compound is diamagnetic, soluble in chloroform, methylene chloride, methanol, ethanol and acetone, insoluble in benzene and light petroleum. m.p.  $215^\circ$ .

Found : C, 66.70; H, 5.19; Cl, 3.80

$\text{C}_{52}\text{H}_{48}\text{ClP}_4\text{Rh}$  requires : 66.77; 5.17; 3.79

Molar conductivity  $10^{-3}$  in nitrobenzene at  $28^\circ$ :  $\Lambda_m = 24.0$

Di- $\{1,2\text{-bis(diphenylphosphino)ethane}\}$ rhodium(I) perchlorate

$[\text{Rh}(\text{C}_2\text{H}_4\{\text{PPh}_2\}_2)_2]\text{ClO}_4$ . A solution of the chloride described above, in ethanol, was treated with an ethanolic solution of sodium perchlorate. The resulting golden-yellow precipitate was collected, washed with ethanol and dried. m.p.  $282^\circ$ .

Found : C, 61.75; H, 4.74; Cl, 3.63

$\text{C}_{52}\text{H}_{48}\text{ClO}_4\text{P}_4\text{Rh}$  requires : 62.49; 4.84; 3.55

Molar conductivity  $10^{-3}$  M in nitrobenzene at  $25^{\circ}$ :  $\Lambda_m = 21.6$ .

Di- $\{1,2\text{-bis(diphenylphosphino)ethane}\}$ rhodium(I) tetraphenylborate

$[\text{Rh}(\text{C}_2\text{H}_4\{\text{PPh}_2\}_2)_2]\text{BPh}_4$ , was similarly prepared from the chloride and sodium tetraphenylborate. Light yellow powder, m.p.  $246^{\circ}$ .

Found : C, 75.3 ; H, 5.76;

$\text{C}_{76}\text{H}_{68}\text{BP}_4\text{Rh}$  requires : 74.88; 5.62.

Molar conductivity  $10^{-3}$  M in nitrobenzene at  $25^{\circ}$ :  $\Lambda_m = 15.7$ .

Hydridodi- $\{1,2\text{-bis(diphenylphosphino)ethane}\}$ rhodium(I)

$[\text{RhH}(\text{C}_2\text{H}_4\{\text{PPh}_2\}_2)_2]$ . a) A solution of  $[\text{Rh}(\text{DPE})_2]\text{Cl}$  (2.0 g, 1 mol) in ethanol (40 cc) was treated with a solution of sodium borohydride (0.24 g, 3 mols) in ethanol (30 cc) under nitrogen. The resulting orange crystalline precipitate was filtered, dried and crystallised from benzene by adding ethanol. Diamagnetic orange plates, m.p.  $242^{\circ}$ , decomp.  $280^{\circ}$ , soluble in benzene, insoluble in ethanol, methanol, light petroleum.

Found : C, 69.25; H, 5.62; P, 14.1

$\text{C}_{52}\text{H}_{49}\text{P}_4\text{Rh}$  requires : 69.33; 5.48; 13.75.

b) A solution of  $[\text{Rh}(\text{DPE})_2]\text{Cl}$  (1.0 g, 1 mol) in tetrahydrofuran (30 cc) was treated with an excess of lithium aluminium hydride in tetrahydrofuran under nitrogen. The original yellow solution rapidly became orange and ethanol was then slowly added until effervescence ceased. The solvent was removed at 6 mm and from the benzene soluble

portion of the residue the orange complex was precipitated with ethanol. The compound was identified by its infrared spectrum.

Deuteridodi- $\left\{1,2\text{-bis(diphenylphosphino)ethane}\right\}$ rhodium(I)

It was similarly prepared in tetrahydrofuran from  $[\text{Rh}(\text{DPE})_2]\text{Cl}$  and lithium aluminium deuteride.

Hydridodi- $\left\{1,2\text{-bis(diphenylphosphino)ethane}\right\}$ cobalt(I)

$[\text{CoH}(\text{C}_2\text{H}_4\{\text{PPh}_2\}_2)_2]$ . was prepared from dibromodi- $\left\{1,2\text{-bis(diphenylphosphino)ethane}\right\}$ cobalt and sodium borohydride both in absolute ethanol, as the corresponding rhodium-derivative, and, according Chatt <sup>(5)</sup>, in 3:1 ethanol-water solution. Diamagnetic red plates, m.p. 237-40°, dec. 280°.

Found : C, 72.8 ; H, 5.86; P, 14.5

$\text{C}_{52}\text{H}_{49}\text{CoP}_4$  requires :      72.90;      5.77;      14.46.

Reactions of the Hydrido-complexes. (1) Reaction with perchloric acid. The hydrido-complex of rhodium (0.1374 g) was treated in an evacuated apparatus with a solution (5 cc) of 1 M perchloric acid in ethanol (80%)-water, and the evolved gas ( 4.00 cc at 20° and 750 mm ) collected. Molar ratio, hydrogen to complex, equal to 1.06. The solid residue, filtered off, washed with ethanol and dried, was identified as di- $\left\{1,2\text{-bis(diphenylphosphino)ethane}\right\}$ rhodium(I) perchlorate by its infrared spectrum, m.p. and analysis. (Found: Cl, 3.72).

(2) Reaction with hydrogen chloride. The hydrido-complex of rhodium (0.1312 g) treated, as described above, with a 1 M solution (5 cc) of

hydrogen chloride in ethanol (80%)-water, gave off hydrogen (3.60 cc at 20° and 750 mm) in a molar ratio hydrogen to complex of 0.997. Another sample of the hydrido-complex (2.0 g), suspended in ethanol (15 cc), was treated with the 1 M solution (10 cc) of hydrogen chloride in aqueous ethanol under nitrogen. After the effervescence ceased, the solvent was removed under vacuum and the residue recrystallized from benzene, yielding a light yellow crystalline compound, m.p. 180-2°, soluble in organic polar solvents, rather soluble in benzene, diamagnetic.

Found : C, 61.15; H, 5.26; Cl, 7.14

$C_{52}H_{49}Cl_2P_4Rh$  requires : 64.27; 5.08; 7.29.

Molar conductivity  $10^{-3}M$  in nitrobenzene at 25° :  $\Lambda_m = 17.8$ .

(3) Reaction with carbon tetrachloride. The hydrido-complexes of rhodium and of cobalt (0.1 g) were treated with carbon tetrachloride (0.25 cc) under nitrogen. After a few minutes, the solvent was distilled under vacuum, collecting it in a dry-ice trap, and its infrared spectrum recorded using 0.1 mm cells and pure carbon tetrachloride as reference. The presence of the chloroform in the solvent was proved by the bands at 1217 and 668  $cm^{-1}$ .

Reaction of di-{1,2-bis(diphenylphosphino)ethane}rhodium(I) chloride with hydrogen chloride. A solution of  $[Rh(DPE)_2]Cl$  (2.0 g) in ethanol (20 cc) was treated as under (2) with a  $1M$  solution of hydrogen chloride in aqueous ethanol (10 cc). After removal of the solvent under vacuum

and recrystallisation of the residue from benzene, the light yellow product was identified by its infrared spectrum, m.p., conductivity in nitrobenzene ( $\Lambda_m = 17.6$  mhos), diamagnetism and analysis (found: C, 62.3; H, 5.18; Cl, 6.97) as the same compound as obtained under (2). By treatment with sodium tetraphenylborate in ethanolic solution, it gave a light yellow precipitate, m.p. 234°, slightly soluble in ethanol.

Found : C, 71.5 ; H, 5.65; Cl, 2.75

$C_{76}H_{69}BCl_4Rh$  requires : 72.64; 5.61; 2.82.

Determination of Dipole Moments. These were determined as described previously <sup>(11)</sup> and are listed in the Table.

	$w_2$	$\Delta\epsilon$	$\Delta v$	$\alpha_0$	$\beta$	$P_T$	$P_E$	$\mu(D)$	$\mu_{20}(D)$
RhH(DPE) <sub>2</sub>	0.01192	0.03305	-0.0049	2.77	-0.41	666.5	274	4.35	4.03
	0.01360	0.03688	-0.0056	2.71	-0.41	656.0	274		
CoH(DPE) <sub>2</sub>	0.00832	0.01877	-0.0037	2.25	-0.45	539.3	274		
	0.00952	0.01954	-0.0044	2.05	-0.46	506.8	274	3.50	3.08

## REFERENCES

- (1) J. Chatt, Proc. Chem. Soc. 1962, 318
- (2) L. Vaska and J.W. DiLuzio, J. Amer. Chem. Soc. 1961, 83, 756  
L. Malatesta, "Advances in the Chemistry of the Co-ordination  
Compounds", ed. S. Kirschner, McMillan Co. New York, 1961, p.475
- (3) J. Lewis, R.S. Nyholm and G.K.N. Reddy, Chem. and Ind. 1960, 1386
- (4) F. Zingales, F. Canziani and A. Chiesa, in press in the "Journ.  
Inorg. Chem."
- (5) J. Chatt, F.A. Hart and D.T. Rosevear, J. 1961, 5504.
- (6) L. Vaska and J.W. DiLuzio, J. Amer. Chem. Soc. 1961, 83, 2784
- (7) L. Vaska. Communication at the Symposium of Inorganic Chemistry.  
June 1963. Cincinnati.
- (8) J. Chatt and B.L. Shaw, J. 1962, 5075
- (9) W.F. Edgell, C. Hagee and G. Gallup, J. Amer. Chem. Soc. 1956, 78, 4185
- (10) J. Chatt and F.A. Hart, J. 1960, 1378
- (11) A. Sacco, Gazz. Chim. It. 1963, 93, 542.

Part II.

" HYDRIDOTRIPHENYLPHOSPHINERHENIUM COMPOUNDS "

by

L. Malatesta, M. Freni and V. Valenti

Summary. Two new complexe hydrides of rhenium with triphenylphosphine are described. The first of these compounds has been fully characterized by chemical means and by NMR spectra as  $\text{ReH}_5\text{L}_3$ .

The second hydride is still uncertain as for the number of hydridic hydrogens. The chemical reactions give results indicating from 5 to 7 hydrogens i.e.  $\text{ReH}_{5-7}\text{L}_2$ , while NMR spectra, on account of the low solubility of this compound could not be qualitatively evaluated.

"HYDRIDOTRI PHENYLPHOSPHINERHENIUM COMPOUNDS"

Freni and Valenti reported some time ago (1) the two hydrido-triphenylphosphinerhenium compounds  $\text{ReH}_3\text{L}_2$  and  $\text{ReH}_3\text{L}_4$  ( $\text{L}=\text{P}(\text{C}_6\text{H}_5)_3$ ). We have now prepared two other rhenium hydrides, belonging to the same class, one of which can be considered  $\text{ReH}_5\text{L}_3$  (I), while we are still uncertain on the number of hydridic hydrogen of the second, which we write for the moment as  $\text{ReH}_n\text{L}_2$  ( $n=5-7$ ).

The hydride (I) is obtained from the benzene solution of  $\text{ReH}_3\text{L}_4$  with excess hydridoborate. It is a yellow crystalline substance, diamagnetic, stable to air and moisture. In benzene solution it behaves as a non electrolyte, shows a molecular weight corresponding to the monomeric formula and an electric moment of about 3,4 D. It is related to (I) in that it can be obtained from it by boiling in benzene solution with an excess of phosphine.

The hydride (II) is formed as a byproduct during the preparation of  $\text{ReL}_2\text{H}_3$ , that is in the reduction of  $\text{ReO}(\text{OC}_2\text{H}_5)\text{I}_2\text{L}_2$  (2) with sodium hydridoborate, and can be obtained in small yields from the mother-liquor. It is a white crystalline substance, stable to air and moisture, diamagnetic. In benzene solution it behaves as a non-electrolyte, with a molecular weight corresponding to the monomeric formula and an electric moment of about 3 D. These solutions decompose slowly on refluxing, with evolution of hydrogen and give  $\text{ReH}_3\text{L}_2$ . The chlorinated solvents decompose (I) and (II) as all the

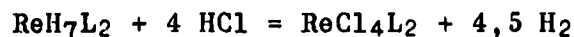
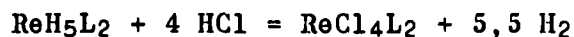
other rhenium hydrides, giving  $\text{ReCl}_4\text{L}_2$ .

The determination of the number of hydridic hydrogen atoms in these compounds is a rather difficult task. The elemental <sup>78</sup> analysis in fact has not enough precision to yield reliable result on this purpose, and the measure of the amount of hydrogen evolved in different conditions, though giving useful results, is partially vitiated. In fact all the reactions reported below are, more or less, accompanied by <sup>by</sup> reactions, in consequence of which their course is far from quantitative.

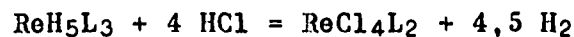
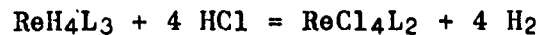
The chemical evidence obtained is the following:

a) The reaction with hydrochloric and hydrobromic acids (HX) gives the tetrahalogenobistriphenylphosphinerhenium compounds,  $\text{ReX}_4\text{L}_2$ , which can be recovered in yield of about 70%, and molecular hydrogen.

In these reactions compound (II) evolved  $5 \pm 0,1$  mol  $\text{H}_2$ , an amount which is intermediate between that required for the reactions:



Compound (I) evolved  $4,0 \pm 0,1$  mol  $\text{H}_2$  in comparison with.



b) The reaction of compounds (I) and (II) with acetic acid did not give any recoverable product and evolved  $4,7 \pm 0,1$  resp.  $3,1 \pm 0,1$  mol  $\text{H}_2$ .

c) In the reaction of these hydrides in xilene with excess iodine, followed by addition of water, the prevailing course apparently is:

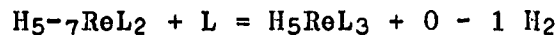


If the reaction was strictly quantitative the equivalents of iodine reduced to hydriodic acid should be function only of the number of L. As a matter of fact this was observed on compound (I) which consumed  $9,9 \pm 0,2$  eq  $\text{I}_2$  (calc. 10 eq) and evolved  $2,1 \pm 0,15$  mol  $\text{H}_2$  (calc. 2,5) but not on compound (II) which consumed  $9,8 \pm 0,1$  eq  $\text{I}_2$  (calc. 8) yielding  $10,0 \pm 0,1$  eq HI (calc. 8) and evolved  $2,8 \pm 0,1$  moles  $\text{H}_2$ .

d) It is well known that the isonitriles give stable complexes with the transition metals in low oxidation state (3) and we thought that all the hydridic hydrogen might be evolved on the reaction of our hydrides (I) and (II) with an excess of tolylisonitrile. As a matter of fact we obtained 2,0 and 2,6 moles  $\text{H}_2$  resp. but these data could not be quantitatively evaluated because we were not able to isolate any definite product from the reaction.

e) When compound (II) was refluxed in xilene it evolved  $1,7 \pm 0,1$  moles  $\text{H}_2$  giving about 70% yield of the well known hydride  $\text{ReH}_3\text{L}_2$ . Compound (II) is stable in these conditions. The same (II) refluxed in benzene with excess of phosphine gave compound (I) (yield 50%) and

1,1 moles  $H_2$ . The main reactions apparently are



but are vitiated by the fact that some complete decomposition of the original hydride <sup>take</sup> also place yielding more hydrogen.

The conclusion which could be drawn from these reactions are:

- 1) Compound (I) shows a number of hydridic hydrogen atoms from 4 to 5 and, being diamagnetic, we consider the figure 5 as more probable.
- 2) Compound (II) shows a number of hydridic hydrogen atoms from 5 to 7.

This chemical evidence has been partially confirmed by NMR spectra.

In the case of compound (II) its solubility in deuterobenzene was rather low and the NMR spectrum could not be quantitatively estimated,

The presence of hydridic hydrogen was confirmed by a triplet at 4,4 ppm (high field positive, tetramethylsilane as internal standard.).

This results rules out the possibility of  $ReH_6L_2$  because we know that (I) is monomeric in benzene solution while paramagnetic behaviour would be required if a even number of hydridic hydrogen atoms was present.

Compound (I), on the other hand, gave in 16% deuterobenzene solution a NMR spectrum characterized by a quartet with a chemical shift of 4,66 ppm (high field positive, tetramethylsilane as internal standard) and a coupling constant  $J_{P-H}$  of 19 c/s. The measure of the areas of the peaks gave an amount of hydridic hydrogen of  $4,8 \pm 0,2$ ,

and as the formula  $\text{ReH}_4\text{L}_3$  can be ruled out, on account of the diamagnetic behaviour of the monomeric solution, as can be deduced from NMR spectrum, the formula  $\text{ReH}_5\text{L}_3$  was confirmed.

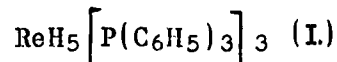
The qualitative result of NMR spectra of the two rhenium hydrides are not easy to interpret. The triplet and the quadruplet could be considered due to the splitting of equivalent hydrogen atoms by two and three equivalent  $^{31}\text{P}$  nuclei resp, but no structure with so high symmetry can be envisaged. On the other hand the electric moment of 3 and 3,4 D are rather low, if we consider that the partial moment phosphine-metal is 4,6 D and the moment hydrogen metal is 0,5 - 1 D. We advance therefore the hypothesis that some averaging process is taking place among the hydrogen atoms.

The behaviour of the complex hydrides of the metals of group eight (4) is very different from that of these rhenium derivatives. The former have in fact well localized hydrogen atoms, giving very strong and well resolved IR stretching bands and showing large chemical shift in NMR spectra. These hydrogen atoms give sometime place to position isomerism and can gradually be substituted with other anionic ligands.

The complex rhenium hydrides so far prepared i.e.  $\text{ReH}_3\text{L}_2$ ,  $\text{ReH}_3\text{L}_4$  (1),  $\text{ReH}_5\text{L}_3$  and  $\text{ReH}_{5-7}\text{L}_2$  on the contrary have hydrido groups which give place to weak and ill resolved IR stretching band, and to low chemical shift in NMR spectra and which cannot be gradually substi-

tuted with anionic ligand. This seems to bring some support to our hypothesis of non localisation of hydridic hydrogen.

EXPERIMENTAL



a) Preparation. 2,0 g  $\text{ReH}_3 \left[ \text{P}(\text{C}_6\text{H}_5)_3 \right]_4$  and 0,2 finely powdered  $\text{NaBH}_4$  suspended in 50 ml benzene were refluxed in nitrogen atmosphere for about one hour. A brown solution formed which was filtered, evaporated to about 20 ml and precipitated by addition of 50 ml ethanol. The yellow crystalline precipitate was filtered (0,9 g) (yield 60%) and recrystallized from benzene + ethanol, m.p.  $162^\circ$ . This compound is stable to air and moisture, very soluble in benzene, nitrobenzene, acetonitrile, acetone, tetrahydrofuran, chloroform and methylene chloride, insoluble in ethanol, ethyl ether and hexane. Solutions in chlorinated solvents decompose slowly giving  $\text{ReCl}_4 \left[ \text{P}(\text{C}_6\text{H}_5)_3 \right]_2$  d.p.  $216^\circ$ .

Found : C 67.0 ; H 5.5 ; P 9.5 ; Re 19.04

$\text{C}_{54}\text{H}_{50}\text{P}_3\text{Re}$  requires : 66.2 ; 5.1 ; 9.5 ; 19.1 .

Magnetic susceptibility (Gouy balance) in the solid state:

$$\chi_m = - 540.10^{-6} \text{ cm}^3/\text{mol}.$$

The diamagnetism in benzene solution can be inferred from the NMR spectrum. Molar conductivity in  $10^{-3}\text{M}$  benzene solution,  $1,06 \text{ ohm}^{-1} \text{ cm}^2$ . Molecular weight in  $10^{-3}\text{M}$  benzene solution (osmometric): Found 944, (calc 973). Electric moment in benzene solution calculated by Enriquez (5) method 3,4 D. The IR spectrum (Infracord 237, nujol mull)

shows two medium broad bands at  $1900\text{ cm}^{-1}$  and  $1970\text{ cm}^{-1}$  ascribable to Re-H stretching and a band of about the same intensity at  $850\text{ cm}^{-1}$  (Re-H bending).

b) Determination of hydridic hydrogen by chemical means.

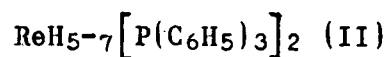
The results are summarized in table I.

TABLE I.

Reagent	H <sub>2</sub> /Re Found	
1) Benzene + HCl	$4,0 \pm 0,1$	(3,90; 4,06; 4,12; 3,81)
2) CH <sub>3</sub> COOH	$3,1 \pm 0,1$	(3,32; 3,0; 2,90)
3) Xilene + I <sub>2</sub>	$2,11 \pm 0,2$	(2,33; 2,19; 2,0 ; 1,92)
4) C <sub>7</sub> H <sub>7</sub> NC	2	(1,8 ; 2,20).

From the mother liquors of reaction 1) (25 ml) containing 1,3 g of compound (I) by addition of 25 ml ethanol we obtained 0,8 g of ReCl<sub>4</sub>L<sub>2</sub> m.p.  $216^{\circ}$  (yield 70%).

The equivalent of iodine consumed in reaction 3) (9,61; 10,19; 9,9 eq) and the hydrogen iodide formed (9,93; 10,5 eq) corresponded roughly to the calculated figure (10 eq).



a) Preparation. A solution of 0,2 g of NaBH<sub>4</sub> in 4 ml 99,4% ethanol is added at room temperature to a saturated benzene solution of 1 g ReO(OC<sub>2</sub>H<sub>5</sub>)[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>. In about one hour a mixture of white and red crystals precipitates, which is filtered and separated

taking advantage of the very high solubility of the white crystals in cold benzene. By addition of ethanol to the benzene solution mg 50 of a silvery-white crystalline compound is precipitated, (yield 6%) very soluble in cold benzene, tetrahydrofuran and carbon disulfide, insoluble in ethanol, acetone, acetonitrile, ethyl ether and hexan. M.p. 140°. The red crystals had previously been recognized (1).

The benzene solution of g 0,1 of (I) turns red on boiling with formation of g 0,07 of  $\text{ReH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , which has confirmed by mixed m.p. and IR spectrum. Chlorinated solvents ( $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ) dissolve the compound, but these solutions are unstable and decompose giving  $\text{ReCl}_4[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , d.p. 216°.

Found : C 59.9 ; H 5.4 ; P 8.76; Re 25.5 ; B not present

$\text{C}_{36}\text{H}_{35}\text{P}_2\text{Re}$  requires : 60.4 ; 4.9 ; 8.68; 26

$\text{C}_{36}\text{H}_{37}\text{P}_2\text{Re}$  requires : 60.2 ; 5.16; 8.66; 25.9 .

Magnetic susceptibility with Gouy balance  $\chi_m = - 380.10^{-6} \text{cm}^3/\text{mol}$ .

Molar conductivity in  $10^{-3}\text{M}$  benzene solution,  $1,55 \text{ohm}^{-1}\text{cm}^2$ .

Molecular weight in  $10^{-3}\text{M}$  benzene solution (osmometric): Found 690, (calc 715-717). Electric moment, determined in benzene and calculated by Enriquez (5) method, 3 D. The IR spectrum (Infracord 237, nujol mull) shows two broad unresolved bands at  $1875 \text{cm}^{-1}$  (Re-H stretching) and  $790 \text{cm}^{-1}$  (Re-H bending).

b) Determination of hydridic hydrogen by chemical means

The results are summarised in the table II:

TABLE II

Reagent	H <sub>2</sub> /Re Found	
1) Xilene + HCl	5,03 ± 0,5	(4,60; 5,63; 5,45; 4,45)
2) CH <sub>3</sub> COOH	4,50 ± 0,33	(4,00; 4,72; 4,75)
3) Xilene + I <sub>2</sub>	2,68 ± 0,12	(2,54; 2,81; 2,65; 2,72)
4) Refluxing benzene	1,57 ± 0,14	(1,52; 1,33; 1,81; 1,62)
5) Refluxing benzene + L	1,12 ± 0,08	(1,25; 1,01; 1,01; 1,1)
6) C <sub>7</sub> H <sub>7</sub> NC	2,6	(2,5; 2,7)

From the mother liquors of reaction 1), (about 25 ml) containing 1,5 g of compound (II) by addition of 25 ml ethanol we could isolate g 1,3 of ReCl<sub>4</sub>L<sub>2</sub>, d.p. 216° (yield 73%). In the reaction 3) we added a known excess of iodine to the xilene solution of the hydride and measured the evolved hydrogen. Then we added some water and titrated first the excess iodine with neutral thiosulphate solution (9,90; 9,85; 9,71; 9,61 eq I<sub>2</sub>) and then the acidity which, within the analytical error, was found equal to the consumed iodine (9,91; 9,72; 9,96; 9,98 eq HI). From reactions 2) and 4) we did not succeed in separating any definite compound.

From the mother liquors of reaction 4) (containing 1,15 g hydride) and of reaction 5) (1,21 g) by addition of ethanol we obtained g 0,9 of ReH<sub>3</sub>L<sub>2</sub> m.p. 168° (yield 80%) and g 1,10 of ReH<sub>5</sub>L<sub>3</sub> m.p. 160° (yield 65%) resp. The identity of these substances was confirmed by their IR spectra and mixed m.p.

References

- (1) M. Freni and V. Valenti, Gazz. Chim. It., 91, 1357 (1961).
- (2) J. Chatt and G.A. Rowe, J. Chem. Soc., 4019, (1962).
- (3) L. Malatesta, Progress in Inorganic Chemistry - Vol. I -  
Ed. by F.A. Cotton, Interscience, New York (1959)
- (4) J. Chatt, Proc. Chem. Soc., 318, (1962).
- (5) P.C. Enriquez, Physica, 1, 41, (1934).
- (6) M. Angoletta, Gazz. Chim. It., 92, 811, (1962).

Part III.

"TRIHYDRIDOTRIS (TRI PHENYLPHOSPHINE) IRIIDIUM COMPOUNDS"

by

Maria Angoletta

Summary. The preparation and properties of the two isomeric forms of  $\text{IrH}_3 [\text{P}(\text{C}_6\text{H}_5)_3]_3$  are described. From dipole moments and IR spectra the high melting isomer is considered to be the trans-form, the low melting the cis-form.

"TRIHYDRIDOTRIS(TRIPHENYLPHOSPHINE)IRIDIUM COMPOUNDS"

A few years ago Chatt (1) observed that the trialkylphosphine derivatives of some metals, belonging to the group VIII of Mendeleieff table, can easily be transformed in hydridohalogentrialkylphosphine metals and in hydridotrialkylphosphine metals. Platinum (1), osmium and rutenium (2) appear to give the most stable compounds, nickel (3) and palladium (4) the least stable.

All these compounds have formulas  $MHXL_4$  or  $MH_2L_4$  ( $X = Cl; Br, I;$   $L =$  trialkylphosphine) and are stable to air. They have well defined composition with probable octahedral structure; the monohydrides are considered to have the hydrogen atoms trans to the halogen and the dihydrides the hydrogen atoms trans each other. These compounds show a very intense absorption band in the IR, at about  $2000\text{cm}^{-1}$ , due to the metal-hydrogen stretching; this band shifts to about  $1400\text{cm}^{-1}$  on deuteration. The NMR absorption (1,2) gives further evidence for the presence of the hydrido atoms.

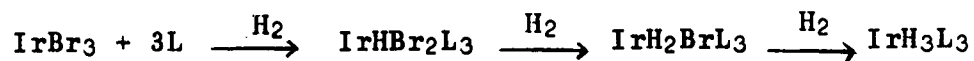
Among the metals of the cobalt group (Co, Rh, Ir) only iridium seems to give stable hydrides: preliminary notes on compounds of this type with triphenylphosphine were made by Malatesta and coworkers, by Hayter (5) and by Vaska (6), while Chatt (7) reported the hydrido complexes with triethylphosphine.

We found now, for the first time, and we succeeded in separating, the two isomeric forms of trihydridotris(triphenylphosphine)iridium,

and we studied the very interesting reaction of these isomers with perchloric acid, as we will describe in following pages.

The transformation of the halogenotriphenylphosphine compounds in the corresponding trihydrides is best carried out using sodium tetrahydridoborate as reducing agent in ethanolic solution or, more exactly, treating with this reagent the suspension obtained by mixing an ethanolic solution of  $\text{IrBr}_3(\text{H}_2\text{O})_x$  with an ethanolic solution of the phosphine:  $\text{P}(\text{C}_6\text{H}_5)_3 = \text{L}$ .

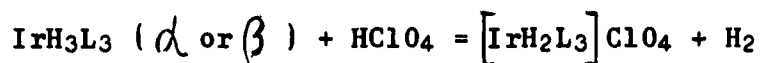
The reaction takes place stepwise:



and, with a defect of reducing agent, the dihydridomonobromocompound can easily be isolated. With an excess of sodium tetrahydridoborate a white crystalline precipitate is readily obtained. This can be separated by fractional crystallisation in two different compounds, which from analysis and properties have been recognized as the two isomers of  $\text{IrH}_3\text{L}_3$ .

The number of hydrogen atoms in these compounds cannot be determined directly by analysis, neither was a reaction found which gave place to the quantitative evolution of all this hydrogen. We have however reached an indirect evidence for the presence of the three hydride atoms. In fact the two hydrides, indicated as  $\alpha$  (high melting form) and  $\beta$  (low melting form) resp., react with dilute perchloric acid in ethanol giving exactly 1 mol of hydrogen and forming the same

perchlorate:



The perchlorate by reaction with NaBr gives by exchange the corresponding bromide in which the presence of two hydrido hydrogens has been proved (6). This compound shows two absorption bands at  $2222 \text{ cm}^{-1}$  and  $2128 \text{ cm}^{-1}$ , which are expected for two hydrogen atoms in non-equivalent positions.

The fact that the two isomers give the same perchlorate is easily explained if we admit that the insaturated cation  $[\text{IrH}_2\text{L}_3]^+$  readily rearranges to give the most stable form.

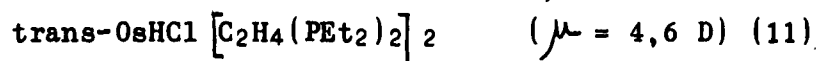
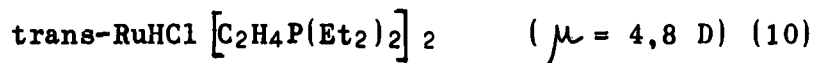
The perchlorate  $[\text{IrH}_2\text{L}_3]\text{ClO}_4$  is a very insaturated compound; in benzenic solution it behaves as an ionic couple with a moment of 13,4 Debey units and in acetone solution as a uni-univalent electrolyte. It easily co-ordinates every kind of ligands ( $\text{NH}_3$ , pyridine, triphenylphosphine, halides ions;  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , etc.), assuming again its coordinative saturation.

The trihydridotriphenylphosphine compounds, with the only exception of the rhenium hydrides (8) which belong to of a quite different type, represent the first case where three hydrogen atoms, bound to the same transition metal, have been observed, and the first case of isomeric hydrides. In fact all the hydrido derivatives of Fe(9), Ru(2), Os(2) and Ir(7), described by Chatt, have been obtained only in one form, neither did Hayter (5) observe, in his preliminary note, that the trihydridotris(triphenylphosphine)iridium is obtained

as a mixture of two isomers.

Evidence for the structure of these isomeric forms has been obtained from their electric moments and from their IR spectra. The measurements made by Chatt (10,11,12) of the electric moment of some hydridophosphine coordination compounds and of some halogeno-carbonylmetals allowed us to make some rough estimation on the electric moment to be expected for the two isomers, and to compare these estimations with the experimental figures. Chatt gives  $\mu = 4,65$  D for the planar compound  $\text{PtCl}_2(\text{CO})_2$  (10) and estimates the Pt-CO bond moment about 0,5 D (Positive end of the moment on CO). From these figures  $\text{Pt-Cl} = (4,65/\sqrt{2}) - 0,5 = 2,8$  D is obtained.

If now we admit that in this type of compounds the metals Ru, Os, Ir and Pt have about the same chlorine-metal moments, from the following figures:



we find for the bond moment M-H a value of  $\mu = 1,4 - 2,0$  D, with the positive end on the hydrogen atom.

The difference between the  $\text{M} \rightarrow \text{P}(\text{C}_6\text{H}_5)_3$  moment, which Chatt estimates as 3,3 - 3,4 D (positive end on the phosphine) and the just calculated bond moment  $\text{M-H} = 1,4 \div 2,0$ , that is  $(4,3 \div 4,4) - (1,4 \div 2) = 2,3 \div 3$  D, should give the moment  $\text{H-Me-P}(\text{Ph})_3$  when the

ligands are at  $180^\circ$ . This is also the moment to be expected for the trans form of  $\text{IrH}_3\text{P}_3$ , if there is no distortion of the octahedron. The experimental determination for the  $\alpha$  - form gave  $\mu = 2,3$  D. The so called  $\alpha$ - form is therefore to be considered the trans form.

The cis isomer, if there are no distortions, should have a moment 1,73 times larger. The bulkiness of the three triphenylphosphine molecules on the same face of the octahedron are likely to give some distortion, so that the calculated figure  $\mu = 3,9$  D  $\div$  5,1 D should be considered a maximum. The value  $\mu = 3,5$  D can be therefore considered in satisfactory agreement with the value calculated for the cis form.

The evidence of the IR spectrum seems to confirm, though not in a rigorous way, the results of the electric moments.

From symmetry considerations two bands should be expected for the (undistorted) cis compound and three for the trans compound, instead of one (at  $2080\text{ cm}^{-1}$ ) and two (at  $1730$  and  $2100\text{ cm}^{-1}$ ) respectively. No conclusion can therefore be derived from the number of these bands. On the other hand we observed that the hexacoordinated hydridophosphine compounds show an absorption at about  $1750\text{ cm}^{-1}$  only when two hydrogen atoms are trans each other. Now the compound which, from the electric moment, is to be considered the trans-trihydridotris-triphenylphosphineiridium shows a band in this region and we consider this should be taken as an additional evidence for the assigned structure.

EXPERIMENTALPreparation of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$ .

20 g  $\text{K}_2\text{IrBr}_6$  (5,14 g Ir; 26,6 moles) in saturated warm aqueous solution were precipitated with 5,6  $\text{Na}_2\text{CO}_3$  (53 moles) and the final pH was adjusted to 7,5. The separated  $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ , washed on a buchner funnel with warm water till the filtrate was free from bromide ions, was dissolved in an excess of 40% aqueous HBr, and evaporated on a w.b. under vacuum. The solid residue was dissolved in methanol, filtered and again evaporated under vacuum. The solid  $\text{IrBr}_3 \cdot n\text{H}_2\text{O}$  was dissolved in about 400 ml ethanol, and the final concentration of this solution, determined on 1 ml, by igniting in a platinum crucible, reducing with hydrogen and weighting, was found to be 0,0101 g Ir/ml.

250 ml of this solution, containing 2,5 g Ir, were added slowly to a solution of 11 g triphenylphosphine in 400 ml ethanol at 60-70°. Then, to the yellow suspension which formed, a saturated solution of 6 g  $\text{NaBH}_4$  in ethanol was slowly added. A very strong evolution of hydrogen took place and the yellow product dissolved slowly while the solution got first very dark, then brown yellow and finally it began to separate a ivory-white crystalline precipitate. The reaction was completed keeping the solution under agitation at about 50° for 1 hour, then the precipitate was filtered and washed first with boiling ethanol, then with hot water, once more with ethanol and finally with hexane. The product was dissolved in methylene chloride and

reprecipitate with ethanol. Yield 9 g. of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$  corresponding to 1.8 g of iridium (about 70%).

On fractional crystallization from benzene + ethanol, two pure fraction could be obtained having the same analysis but different IR spectra and m.p.s, which we considered isomers. We called  $\alpha$  the less soluble, more abundant isomer and  $\beta$  the other. The  $\alpha$  isomer formed plate-like crystals soluble in benzene; methylene chloride, tetrahydrofuran m.p. 170-173° on air and 220° in vacuum. The IR spectrum in nujol showed a very strong band at 1730  $\text{cm}^{-1}$  and a medium band at 2100  $\text{cm}^{-1}$ .

Found : C 66.2 ; H 4.35; Ir 20.4 ; P 9.15

$\text{C}_{54}\text{H}_{48}\text{IrP}_3$  requires : 66.2 ; 4.9 ; 19.7 ; 9.5 .

The  $\beta$  isomer which formed needle-like crystals, was somewhat more soluble than the  $\alpha$  isomer, m.p. 150° on air and 217° in vacuo.

Found : C 67.0 ; H 4.76; Ir 20.6 ; P 9.3 .

#### Reactions with $\text{HClO}_4$

To 1 g of the  $\alpha$  isomer in 20 ml ethanol, 10 ml of a 10% ethanol solution of  $\text{HClO}_4$  were added. The solution was gently warmed till the most part of crystals was dissolved, and then filtered. On cooling it separated prismatic crystals which were recrystallized from benzene (Perchlorate A) m.p. 140°. When the same reaction was carried out with the  $\beta$  isomer, a perchlorate B was obtained m.p. 140° apparently

identical with A.

Found A: C 59.78; H 4.39; Cl 3.26

" B: 59.60; 4.20; 3.30

$C_{54}H_{47}ClIrO_4P_3$  requires: 60.0 ; 4.15; 3.26.

The IR spectra of the two isomers are identical and show two bands at  $2222\text{ cm}^{-1}$  and  $2128\text{ cm}^{-1}$ .

Molar conductivity in  $2.7 \cdot 10^{-3}M$  benzene  $\Delta = 117$ ; in  $1.7 \cdot 10^{-4}M$  solution  $\Delta = 143$ .

Electric moment. To determined the electric moment the total polarization was calculated in benzene solution using this formula:

$$P_{\infty} = \frac{3\alpha V_1 M_2}{(\epsilon_1 + 2)^2} + M_2 (V_1 + \beta) \frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

TABLE I

Compounds	$\omega_2$	$\Delta\epsilon$	$\alpha$	$\beta$	$R_D$	$P_{\infty}$	$P_0$	D
$\alpha IrH_3 [P(C_6H_5)_3]_3$	0.01841	0.01830	0.994	0.4898	266	375	109	2,3
$\beta IrH_3 [P(C_6H_5)_3]_3$	0.01646	0.02957	1.797	0.4898	266	524	258	3,5
$IrH_2 [P(C_6H_5)_3]_3 ClO_4$	0.01817	0.3706	18.35	0.4898	276	3496	3217	13,4

$M_2$  = mol. weight of solute;  $\omega_2$  = weight fraction of solute

$V_1$  = mol. volume of solvent;  $V_2$  = mol. volume of solution

$\epsilon_1$  = dielectric constant of solvent;  $\epsilon_2$  = dielectric constant of solution

$R_D$  = calculated Molar refraction for D line.

$$\alpha = \frac{\Delta\epsilon}{\omega_2}; \quad = \frac{\Delta V}{\omega_2}; \quad \Delta\epsilon = \epsilon_2 - \epsilon_1; \quad \Delta V = V_2 - V_1; \quad P_0 = P_{\infty} - R_D$$

References

- (1) J. Chatt, L.A. Duncanson and B.L. Shaw, Proc.Chem.Soc.,1957,343
- (2) J. Chatt and R.G. Hayter, J. Chem. Soc., 1961, 2605
- (3) M.L.H Green, H. Street and G. Wilkinson, Z. Naturforsh,14 B,738(1959)
- (4) J. Chatt, L.A. Duncanson and L.B. Shaw, Chem. and Ind.  
1958, 859; Proc. Chem. Soc., 1957, (343)
- (5) R.G. Hayter, J. Am. Chem. Soc. 83, 1259 (1961)
- (6) L. Vaska, J. Am. Chem. Soc. 83, 756 (1961)
- (7) J. Chatt, Proc. Chem. Soc. 1962, 321
- (8) A.P. Ginsberg, J.M. Miller and E.Koubet, J.Am.Soc. 85,4909(1961)
- (9) J. Chatt and R.G. Hayter, J. Chem. Soc. 1961, 6607
- (10) J. Chatt and A.A. Williams, J. Chem. Soc. 1951, 3061
- (11) J. Chatt and R.G. Hayter, J. Chem. Soc. 1961, 2605
- (12) J. Chatt and F.A. Hart, J. Chem. Soc. 1961, 1378.

Part IV.

"SUBSTITUTION DERIVATIVES OF TRIHYDRIDOTRIS(Ph)PHOSPHINEIRIDIUM"

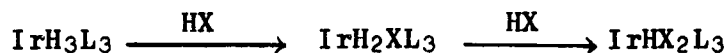
by

M. Angoletta and A. Araneo

Summary. New derivatives of trihydridotris(phenyl)phosphine-iridium with hydrogen halides, halogens, oxoacids and organic acids, are described. The reactions between dihydridotris(phenyl)phosphine-iridium perchlorate with neutral and anionic ligands, involving either addition or substitution, are studied.

"SUBSTITUTION DERIVATIVES OF TRIHYDRIDOTRIS(TRIPHENYLPHOSPHINE)IRIDIUM"

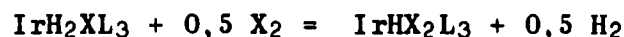
Between the more interesting and characteristic reactions of  $\text{IrH}_3\text{L}_3$  (1) [where  $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ ] we found those with halogen acids and halogens, to give different halogenated compounds. Hydrochloric and hydrobromic acids reacted according to the following pattern, hydrogen being evolved:



On the contrary, in the reaction with hydroiodic acid, when the second hydrogen atom was substituted, one mole of phosphine was lost:



On reacting chlorine or bromine (1 or 2 equivalents), almost the corresponding quantity of hydrogen was evolved, while only a trace of halogen acid was formed:



On using a larger quantity of halogen, one mole of phosphine was displaced first and then the last hydrogen atom was removed:



With iodine an analogous reaction was observed; but  $\text{IrHI}_2\text{L}_3$  could not be isolated, in that it was converted at once to  $\text{IrHI}_2\text{L}_2$ , losing one mole of phosphine, and so the two above mentioned reactions occurred simultaneously:



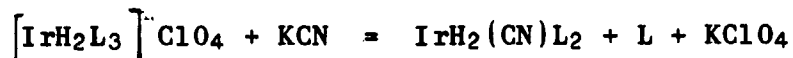
An excess of iodine was found necessary to remove the last hydrogen atom: periodides were then formed, the formulae of which depended on the excess of iodine. Because periodide ion is not generally found to be a coordinating ligand, we thought it should give place to a salt-like structure, as  $[\text{IrI}_2\text{L}_2]\text{I}_3$ ; which actually was proved by conductivity measurements.

Organic acids reacted in a different way, that is only one hydrogen atom was substituted. This happened also when a dicarboxylic acid was used and it was also impossible to form a chelate ring. These products (acetate, hydrogenmalonate, hydrogenoxalate) are crystalline compounds and are soluble in non-electrolyte organic solvents. Their IR spectra (nujol mull) showed two bands, at about  $1900 \text{ cm}^{-1}$ , which could be assigned to the stretching frequencies of Ir-H bond; besides, the usual bands associated with carboxylic groups could be seen. These organic acid derivatives did not behave as salt-like substances; however, the bond between the iridium atom and the oxygen atom of the carboxylic group is rather labile, so that the organic anion could be readily replaced by halide, nitrite, nitrate ions etc.

The most interesting compound among those obtained through acid substitution on  $\text{IrH}_3\text{L}_3$  was however the perchlorate, the preparation of which had been previously (1) described.

The cation  $[\text{IrH}_2\text{L}_3]^+$  of this salt-like compound behaved as a

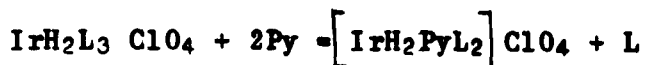
strongly unsaturated substance, It reacted with anionic ligands giving neutral, hexacoordinate complexes, e.g.:  $\text{IrH}_2\text{XL}_3$ , where X means Cl, Br, I,  $\text{NO}_2$ ,  $\text{NO}_3$ . It also added CN, but, in this case, simultaneously, one mole of phosphine was lost to give a new very stable pentacoordinate complex:



On reacting the perchlorate with alcoholic potassium hydroxide the trihydrido-compound  $\text{IrH}_3(\text{PR}_3)_3$  was re-obtained (both  $\alpha$  and  $\beta$  isomers) together with a trace amount of a carbonyl-hydride  $\text{IrHCOL}_3$  (2).

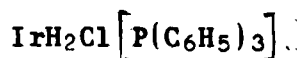
Salts of the saturated complex cation  $[\text{IrH}_2\text{L}'\text{L}_3]^+$  were obtained on adding neutral ligands L' to the perchlorate. When triphenylphosphine was used,  $[\text{IrH}_2\text{L}_4]\text{ClO}_4$  was obtained which, contrary to  $[\text{IrH}_2\text{L}_3]\text{ClO}_4$ , was very sparingly soluble in benzene and chloroform. By action of alcoholic potassium hydroxide on  $[\text{IrH}_2\text{L}_4]\text{ClO}_4$  we did not obtain the expected  $\text{IrHL}_4$  (the analogous compound  $\text{IrHCOL}_3$ , which has one CO group in place of a phosphine, is very stable (2)), but on the contrary here also a mixture of the isomers of  $\text{IrH}_3\text{L}_3$  and a trace of  $\text{IrHCOL}_3$  (2) formed. With ammonia the complex  $[\text{IrH}_2(\text{NH}_3)\text{L}_3]\text{ClO}_4$  was obtained, the electric moment of which was found to be not very different from that of the starting perchlorate (14,1 and 13,4 D respectively) (1).

A somewhat different reaction was observed when piridine (Py) was reacted: one mole of phosphine was removed and dihydridobistriphenylphosphineiridium perchlorate was obtained:



In a similar way, 1,2-bis(diphenylphosphino)ethane reacted with displacement of one mole of phosphine and likely formation of a chelate ring.

EXPERIMENTAL



a) -  $\text{IrH}_3 \left[ \text{P}(\text{C}_6\text{H}_5)_3 \right]_3$  (1,0 g) in benzene (100 ml) was reacted with excess methanolic HCl. After boiling for a few minutes, on cooling, a pale yellow compound crystallized out: m.p. 163°C, soluble in methylene chloride and chloroform, little soluble in benzene. IR bands at 2180 and 2135  $\text{cm}^{-1}$ .

b) -  $\text{IrH}_3 \left[ \text{P}(\text{C}_6\text{H}_5)_3 \right]_3$  (1,0 g) was dissolved in  $\text{CHCl}_3$  (30 ml) and the solution was refluxed for 24 hours. After taking off the solvent till the volume of the solution was 10 ml on adding ethanol, 0,8 g of pale yellow crystals were obtained, identical to the above compound.

Found a): C 63.9 ; H 4.8 ; Cl 3.5 ; Ir 19.0

b): 63.7 ; 4.7 ; 3.5 ; 19.1

for  $\text{C}_5\text{H}_4\text{ClIrP}_3$  calc: 63.8 ; 4.6 ; 3.5 ; 19.0



$\text{IrH}_3 \left[ \text{P}(\text{C}_6\text{H}_5)_3 \right]_3$  (1,0 g) was dissolved in benzene (50 ml) and a HCl stream was bubbled through the solution for 1 hr at 60°C. On adding ethanol pale yellow crystals were obtained (0,7 g), crystal-

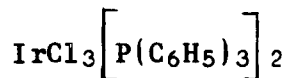
lized from benzene-ethanol, m.p. 145°C; soluble in benzene, chloroform, methylene chloride and tetrahydrofuran. IR bands at 2200  $\text{cm}^{-1}$ .

Found: C 63.9 ; H 4.9 ; Cl 6.5 ; Ir 17.1 ; P 8.4  
for  $\text{C}_{60}\text{H}_{53}\text{Cl}_2\text{IrP}_3$  calc: 63.7 ; 4.7 ; 6.27; 17.0 ; 8.24.

A compound as above, but without crystallization solvent, i.e.

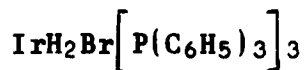
$\text{IrHCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3$  was obtained when a tetrahydrofuran solution (50 ml) of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$  (1 g) was boiled for 1 hr with 10 ml concentrated hydrochloric acid, the solution concentrated and ethanol added. IR stretching frequency at 2200  $\text{cm}^{-1}$  (Ir-H).

Found: C 63.5 ; H 5.5 ; Cl 6.80; Ir 18.5  
for  $\text{C}_{54}\text{H}_{46}\text{Cl}_2\text{IrP}_3$  calc: 61.7 ; 5.37; 6.74; 18.3 .



A solution of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$  (1.0 g) in carbon tetrachloride (50 ml) was treated with a solution of chlorine in carbon tetrachloride (6 equivalents in 20 ml) affording yellow crystals, which were recrystallized from methylene chloride plus methanol, m.p. 189-195°C. No band could be observed in the hydride region of its IR spectrum.

Found: C 51.8 ; H 4.1 ; Cl 12.9 ; Ir 23 ; P 7.4  
for  $\text{C}_{36}\text{H}_{30}\text{Cl}_3\text{IrP}_2$  calc: 52.4 ; 3.65; 12.9 ; 23.3; 7.53.



An ethanolic suspension (50 ml) of  $\text{IrH}_2(\text{OOC-COOH})[\text{P}(\text{C}_6\text{H}_5)_3]_3$  (1,0 g)

was treated with sodium bromide (0,2 g). After boiling for a few minutes the solvent was taken off; the residue was extracted with benzene; on adding ethanol to the filtered solution pale yellow crystals were obtained (0,6 g), m.p. 168°C (with dec.); soluble in benzene, acetone, chloroform and methylene chloride. IR bands at 2230 and 2280  $\text{cm}^{-1}$ .

Found: C 61.7 ; H 4.7 ; Br 7.5 ; Ir 18.2 ; P 8,5  
 for  $\text{C}_{54}\text{H}_{47}\text{BrIrP}_3$  calc: 61.12; 4.45; 7.55; 18.2 ; 8.77.  
 Molecular weight, osmometric in benzene solution (2%): 1060, calc. 1061.



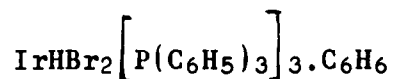
a) A solution of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$  (1,0 g) in benzene (50 ml) was treated with bromine (2 equivalents), in chloroform. On adding ethanol pale yellow crystals were obtained (0,7 g); after crystallization from benzene plus ethanol m.p. 152°C; soluble in benzene, chloroform and methylene chloride.

b) A suspension of 1 g of  $\text{IrHBr}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$  in 100 ml benzene was treated with 1 g of  $\text{P}(\text{C}_6\text{H}_5)_3$  and refluxed for about 3 hours till the solution became clear. On adding ethanol rhomboidal pale yellow crystals separated, m.p. 152°C.

c) To a solution of 4 g  $\text{P}(\text{C}_6\text{H}_5)_3$  in 50 ml ethanol a saturated solution of 1 g  $\text{IrBr}_3 \cdot \text{aq}$  was added in ethanol while boiling. On refluxing for about 1 hour yellow crystalline precipitate is slowly formed

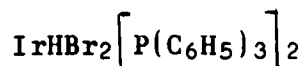
(1,3 g) which after crystallization from benzene plus ethanol melted at 152°C. Compounds a) b) and c) had the same IR spectrum with a stretching Ir-H band at 2200  $\text{cm}^{-1}$ .

Found a): C 58.1 ; H 4.1 ; Br 14.7 ; Ir 17.4 ; P 8.5  
 b): 57.5 ; 4.1 ; 14.8 ; 17.2 ; 8.7  
 c): 57.5 ; 4.2 ; 14.5 ; 17.3 ; 8.6  
 for  $\text{C}_{54}\text{H}_{46}\text{Br}_2\text{IrP}_3$  calc: 57.0 ; 4.03; 14.05; 16.86; 8.15.



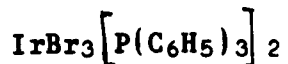
An HBr stream was bubbled for 15' through a benzene solution (50 ml) of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$  (1,0 g) at 50°C. After concentration a yellow compound was obtained (0,6 g) which after crystallization from benzene had m.p. 167°C. IR band at 2220  $\text{cm}^{-1}$ .

Found: C 58.9 ; H 4.9 ; Br 13.9 ; Ir 15.5  
 for  $\text{C}_{60}\text{H}_{52}\text{Br}_2\text{IrP}_3$  calc: 59.16; 4.30; 13.15; 15.78.



A benzene solution (50 ml) of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$  (1,0 g) was treated with bromine (4 equivalents) in carbon tetrachloride. On adding ethanol pale yellow needles separated out, m.p. 213°, soluble in chloroform and methylene chloride. IR band at 2250  $\text{cm}^{-1}$ .

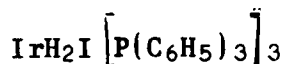
Found: C 47.91; H 3.9 ; Br 18.2 ; Ir 21.5 ; P 6.8  
 for  $\text{C}_{36}\text{H}_{31}\text{Br}_2\text{IrP}_2$  calc: 49.36; 3.56; 18.2 ; 21.9 ; 7.06.



1 g of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$  was suspended in ethanol (30 ml) and an excess of bromine (5,5 equivalents) was added. Yellow needles separated, which after crystallization from methylene chloride plus methanol melted at 162°C; soluble in methylene chloride and chloroform.

No Ir-H band could be observed in its IR spectrum.

Found: C 43.9 ; H 3.2 ; Br 25.2 ; Ir 20.1 ; P 6.8  
for  $\text{C}_{36}\text{H}_{30}\text{Br}_3\text{IrP}_2$  calc: 45.4 ; 3.17; 25.1 ; 20.01; 6.48.

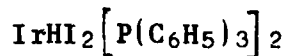


a) A solution of 1 g of  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$  in benzene (100 ml) was treated with iodine (1 equivalent) in benzene (25 ml). On concentrating and on adding ethanol yellow crystals separated, which, after recrystallization from benzene plus ethanol, melted at 190°; soluble in benzene, chloroform, methylene chloride and tetrahydrofuran. IR bands at 2210 and 2080  $\text{cm}^{-1}$ .

b) An ethanolic solution (50 ml) of 1 g  $\text{IrH}_2(\text{OOCCH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_3$  was treated with sodium iodide (0,5 g). After boiling for 1 hour yellow crystals were obtained (0.8 g).

c) A solution of 2,5 g  $\text{IrH}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3$  ( $\text{ClO}_4$ ) in 250 ml ethanol was treated with sodium iodide (0,5 g). Yellow needlelike crystals were formed immediately (2 g). The compounds obtained in a) b) and c) were recognized as identical, from mixed m.p. and IR spectra.

Found a): C 57.4 ; H 4.5 ; I 11.9 ; Ir 17.1  
 b): 58.0 ; 4.8 ; 12.0 ; 17.4  
 c): 58.7 ; 4.5 ; 11.8 ; 17.0  
 for  $C_{54}H_{47}I_2IrP_3$  calc: 58.5 ; 4.28; 11.4 ; 17.30.



a) A benzene solution (100 ml) of  $IrH_3[P(C_6H_5)_3]_3$  (1,0 g) was refluxed with a solution of iodine (4 equivalents) for 1 hour. The yellow crystals were recrystallized from chloroform plus ethanol: 0,6 g, m.p. 220°C. IR band at 2270  $cm^{-1}$ .

b) 1 g  $IrCl_2H[P(C_6H_5)_3]_3$  was suspended in 50 ml acetone and treated with excess NaI. After boiling a few minutes, a yellow crystalline compound (0,5 g) separated m.p. 220°C, soluble in chloroform and methylene chloride, identical to compound above.

Found a): C 43.6 ; H 4.0 ; I 26.0 ; Ir 20.5  
 b): 44.2 ; 3.3 ; 26.1 ; 19.8  
 for  $C_{36}H_{31}I_2IrP_2$  calc: 44.5 ; 3.22; 26.2 ; 19.7 .



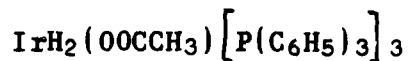
1 g of  $IrH_3[P(C_6H_5)_3]_3$  was suspended in ethanol (50 ml); iodine (7 equivalents) in benzene was added; after boiling for 5' on adding ethanol reddish-brown crystals, m.p. 168°C, separated.

Molecular conductivity in nitrobenzene solution ( $10^{-3}M$ ) at 25°C :

$$\Delta = 16 \text{ ohm}^{-1} \text{ cm}^2.$$

No Ir-H band could be found in its IR spectrum.

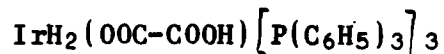
Found: C 31.9 ; H 2.2 ; I 46.8 ; Ir 14.4 ; P 4.5  
for  $C_{36}H_{30}I_5IrP_2$  calc: 31.95; 2.35; 47.3 ; 14.2 ; 4.58.



A suspension of 1 g of  $IrH_3[P(C_6H_5)_3]_3$  in glacial acetic acid (20 ml) was heated on water bath to complete solution. On cooling colourless crystals separated, which were crystallized from benzene ethanol: m.p. 180°C; non electrolyte in nitrobenzene.

IR bands at 2125 and 2170  $cm^{-1}$ .

Found: C 64.6 ; H 4.6 ; Ir 18.6 ; P 8.15  
for  $C_{56}H_{50}IrO_2P_3$  calc: 64.5 ; 4.84; 18.6 ; 8.92.



1 g of  $IrH_3[P(C_6H_5)_3]_3$  was dissolved in 50 ml tetrahydrofuran and oxalic acid (1.0 g) was added. After heating for 1 hour, methanol was added and white crystals separated; m.p. 184°C, soluble in tetrahydrofuran, benzene, chloroform and methylene chloride.

IR bands at 2210 and 2260  $cm^{-1}$ .

Found: C 62.9 ; H 4.4 ; Ir 18.3 ; P 8.6  
for  $C_{56}H_{48}IrO_4P_3$  calc: 62.8 ; 4.54; 17.9 ; 8.7 .



1 g of  $IrH_3[P(C_6H_5)_3]_3$  was dissolved in benzene (100 ml), malonic

acid (0,8 g) dissolved in ethanol was added and the solution was heated till no more gas was evolved. On concentrating white crystals (0,8 g) separated; soluble in benzene, ethanol, acetone, chloroform and methylene chloride. IR bands at 2190 and 2195  $\text{cm}^{-1}$ .

Found: C 63.39; H 4.85; Ir 17.8

for  $\text{C}_{57}\text{H}_{50}\text{IrO}_4\text{P}_3$  calc: 63.1 ; 4.65; 17.7 .



To a solution of  $\text{IrH}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{ClO}_4$  (1,0 g) in benzene (20 ml) triphenylphosphine (0,3 g) was added; an amber-yellow oil was obtained which was dissolved in ethanol; on concentration ivory-white crystals separated: m.p. 207-208°C (under vacuum, with decomposition); soluble in acetone, tetrahydrofuran, sparingly soluble in benzene and ethanol. Molar conductivity in  $10^{-3}\text{M}$  acetone solution at 25°C:  $\Lambda = 123.5 \text{ ohm}^{-1}\text{cm}^2$ . IR bands at 2250 and 2225  $\text{cm}^{-1}$ .

Found: C 62.9 ; H 4.4 ; Cl 2.7 ; Ir 13.9

for  $\text{C}_{72}\text{H}_{62}\text{ClIrO}_4\text{P}_4$  calc: 64.4 ; 4.65; 2.64; 14.3 .



0,5 g of  $\text{IrH}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3 \text{ClO}_4$  were dissolved in ethanol (50 ml) and few ml ethanolic ammonia were added. On cooling colourless plates precipitated: m.p. 233-34°C (under vacuum, with decomposition). Molar conductivity  $10^{-3}\text{M}$  nitrobenzene solution at 30°C:  $\Lambda = 20,8 \text{ ohm}^{-1}\text{cm}^2$ . IR bands at 2148 and 2152  $\text{cm}^{-1}$ .

Found: C 58.2 ; H 4.8 ; Cl 3.20; Ir 17.1; N 1.3

for  $C_{54}H_{50}ClIrNO_4P_3$  calc: 59.0 ; 4.6 ; 3.22; 17.5; 1.2.

Electric moment. To determine the electric moment the total polarization was calculated in benzene solution using this formula:

$$P_{\infty} = \frac{3dV_1M_2}{(\epsilon_1+2)^2} + M_2(V_1+\beta)\frac{\epsilon_1-1}{\epsilon_1+2}$$

TABLE I

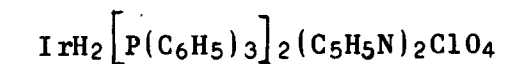
Compound	$\omega_2$	$\Delta\epsilon$	$\alpha$	$\beta$	$R_D$	$P_{\infty}$	$P_0$	D
$IrH_2(NH_3)[P(C_6H_5)_3]_3ClO_4$	0,018299	0,3706	20,25	0,4898	285	4396	4111	14,1

$M_2$  = molecular weight of the solute;  $\omega_2$  = weight fraction of the solute

$V_1$  = molecular volume of the solvent;  $V_2$  = molecular vol. of the solution

$\epsilon_1$  = dielectric constant of the solvent;  $\epsilon_2$  = dielec. const. of the solution

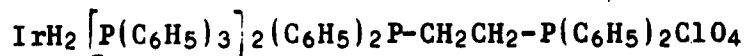
$$\alpha = \frac{\Delta\epsilon}{\omega_2}; \beta = \frac{\Delta}{\omega_2}; \Delta\epsilon = \epsilon_2 - \epsilon_1; \Delta V = V_2 - V_1; P_0 = P_{\infty} - R_D$$



An ethanolic of 1,5 g  $IrH_3[P(C_6H_5)_3]_3ClO_4$  was treated on water bath with pyridine (0,5 g) yielding a crystalline compound (0,2 g); which after crystallization from ethanol, melted at 224-6°C (under vacuum). IR bands at 2150 and 2155  $cm^{-1}$ .

Found: C 56.2 ; H 4.4 ; Ir 18.5 ; N 2.9

for  $C_{46}H_{42}ClIrN_2O_4P_2$  calc: 56.5 ; 4.3 ; 19.6 ; 2.86.

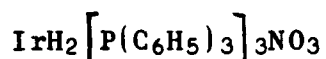


An ethanolic solution of  $IrH_2[P(C_6H_5)_3]_3ClO_4$  (1,5 g) was treated

with  $(C_6H_5)_2P-CH_2CH_2-P(C_6H_5)_2$  (0,5 g) and then refluxed till a clear solution was obtained. After a few hours colourless crystals precipitated m.p. 182-184°C with decomposition. IR bands at 2100 and  $2150\text{ cm}^{-1}$ .

Found: C 61.5 ; H 4.7 ; Cl 2.9

for  $C_{62}H_{56}ClIrO_4P_4$  calc: 61.2 ; 4.6 ; 2.92.



a) An ethanol solution of  $IrH_2[P(C_6H_5)_3]_3ClO_4$  (0,5 g) was treated with a few drops of concentrated nitric acid, affording a crystalline ivory-yellow precipitate, m.p. 199°C.

Molal conductivity in  $10^{-3}M$  acetone solution:  $\Lambda = 110\text{ ohm}^{-1}\text{cm}^2$ .

IR band at  $2180\text{ cm}^{-1}$ .

The same compound could be obtained as follows:

b) A saturated ethanol solution of  $IrH_2[P(C_6H_5)_3]_3ClO_4$  was treated with lithium nitrate, dissolved in ethanol.

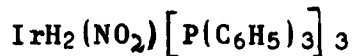
c) A saturated solution of  $IrH_3[P(C_6H_5)_3]_3$  was treated with a few drops of concentrated nitric acid gently warmed on water bath for a few minutes and then cooled.

Found a): C 62.7 ; H 4.4 ; Ir 18.8 ; N 1.4

b): 62.3 ; 4.2 ; 18.1 ; 1.37

c): 62.4 ; 4.3 ; 18.0 ; 1.5

for  $C_{54}H_{47}IrNO_3P_3$  calc: 62.0 ; 4.5 ; 18.5 ; 1.34.

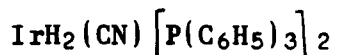


Excess sodium nitrite ( $\approx 0,5$  g) was added to a methanolic solution (100 ml) of  $\text{IrH}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{ClO}_4$  (1,7 g) which was then refluxed for about 1 hour. On cooling colourless crystals were obtained (1,4 g); m.p. 141-143°C.

IR bands at 2130 and 2180  $\text{cm}^{-1}$ .

Found: C 62.9 ; H 4.4 ; Ir 19.7 ; N 1.4

for  $\text{C}_{54}\text{H}_{47}\text{IrNO}_2\text{P}_3$  calc: 63.1 ; 4.55; 18.42; 1.34.



A methanol solution (30 ml) of  $\text{IrH}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{ClO}_4$  (0,8 g) was treated with potassium cyanide (0,157 g) 1 mole. On evaporating the solution a crystalline compound was obtained, which, after recrystallization from methanol, melted at 231-34°C; soluble in methanol and ethanol.

IR bands at 2090-2180 (Ir-H) and 2000  $\text{cm}^{-1}$  (CN)

Found: C 58.6 ; H 5.1 ; Ir 25.7 ; N 1.7

for  $\text{C}_{37}\text{H}_{32}\text{IrNP}_2$  calc: 59.7 ; 4.3 ; 25.9 ; 1.88.

#### References

- (1) This Report, part III.
- (2) This Report, part V.

Part V.

" NEW HYDRIDO AND CARBONYLHYDRIDOIRIDIUM COMPLEXES "

by

L. Malatesta and M. Angoletta

Summary. The preparation and properties a four new complexe iridium-hydrides i.e.  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ ,  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ ,  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  and  $\text{IrH}_3\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  are described. The relationships among these compounds and their derivatives are studied.

"NEW HYDRIDO AND CARBONYLHYDRIDOIRIDIUM COMPLEXES"

The iridium complex hydrides so far reported, belong to the type  $\text{IrH}_3\text{L}_3$  where L may be triphenylphosphine (1) or the diethylphenylphosphine (2). Using as ligand triphenylphosphine we have now prepared the non saturated hydride  $\text{IrH}_3\text{L}_2$  (I), as well as three hydridocarbonylphosphineiridium compounds i.e.  $\text{IrHCOL}_2$  (II);  $\text{IrH}_3\text{COL}_2$  (III) and  $\text{IrHCOL}_3$  (IV).

The trihydridobistriphenylphosphineiridium I was prepared by reduction both with sodium tetrahydridoborate and with lithium tetrahydridoaluminate of  $[\text{IrI}_2\text{L}_2]\text{I}_3$  or  $\text{IrI}_2\text{HL}_2$ . It is a white powder, stable to air and moisture, almost insoluble in all solvents, diamagnetic. The number of hydridic hydrogen atoms, which as usual can not be determined by analysis only, was proved by the reaction with triphenylphosphine, which gives place very rapidly in the cold to the two isomeric forms of the well known trihydride:



The very low solubility of compound (I), could have been ascribed to polymerisation in the solid, through tricenter hydrogen bonds, but this was disproved by the fact that it has only one very strong absorption band in the IR at  $1945 \text{ cm}^{-1}$ , that is in the region characteristic for simple metal-hydrogen bonds. This band could be unequivocally assigned to Ir-H stretching, because it moves to 1360 in the corresponding deuteride.

A structure of compound (I) consistent with the presence of only one hydrogen stretching band is that of a trigonal bipyramid with the two phosphine at the apices and the hydrogen atoms in the equatorial plane. We consider therefore provisionally this structure as the more probable for this hydride.

Compound (I) reacted in very mild condition with pyridine giving the saturated hydride  $\text{IrH}_3\text{LPy}$  which has two strong bands in the infrared at 1700 and  $2120\text{ cm}^{-1}$ . These two bands are very similar to the bands of the  $\alpha$  form of  $\text{IrH}_3\text{L}_3$  (1), for which we proposed a structure with 2 hydrogen atoms trans each other. We suggest that in this case too the trans isomer is formed.

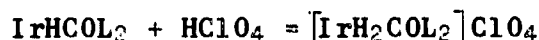
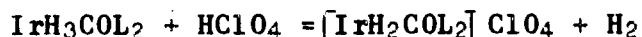
A reaction of (I), which at first puzzled us, was observed with carbon monoxide, which was adsorbed but did not form the expected trihydride  $\text{IrH}_3\text{COL}_2$ , but on the contrary formed the monohydride  $\text{IrHCOL}_2$ . When we proved however that the former changes easily into the latter in solution as said below, this apparent contradiction was completely explained.

The reaction of carbon monoxide on  $\text{IrH}_3\text{L}_2$  prompted us to study the hydridocarbonyltritriphenylphosphineiridium compounds. The reduction of  $\text{IrClCOL}_2$ , described by Vaska (3) and of  $\text{IrHI}_2\text{COL}_2$ , prepared by ourselves, with sodiumhydrideborate gave the same white substance, soluble in organic solvent, moderately stable, melting at  $146^\circ$ . The analysis of this substance corresponded fairly well to the formula

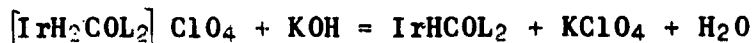
IrH<sub>x</sub>COL<sub>2</sub> but its IR spectrum was rather puzzling in that<sup>it</sup> had 5 bands in the region characteristic for Ir-H and CO stretching, the intensity of which changed on recrystallizing. After several recrystallization, however we obtained a rather simple spectrum with only two strong bands at 1960 and 2000 cm<sup>-1</sup>. We made then the hypothesis that the original hydride was the trihydride IrH<sub>3</sub>COL<sub>2</sub> (III) impure with some IrHCOL<sub>2</sub> (II), and that on recrystallization a mole of hydrogen was slowly lost.

This hypothesis was proved in two different ways: 1) The solution of the hydride (II), by action of molecular hydrogen, at ordinary temperature and pressure formed again the trihydride (III) (NaBH<sub>4</sub> gives the same reaction).

2) The monohydride (II) reacted with perchloric acid, without any evolution of hydrogen, giving a perchlorate which was found identical with the perchlorate obtained from the trihydride with the evolution of one mole hydrogen:



The perchlorate obtained by both ways, gave with one equivalent of potassium hydroxyde the monohydride (II):



The trihydride (III) has three very strong bands in the IR, at 1785, 1965 and 2080 cm<sup>-1</sup>. The first of these bands, which is also the strongest, falls in the region which seems to be characteristic of

compounds having two hydrogens in trans to each other (1). This compound, therefore, deriving from a  $d^6$  low spin hexacoordinated iridium (III) can be considered to have a octahedral structure, corresponding to that of the trans-trihydridotristriphenylphosphine-iridium (1) with a CO ligand in the place of a triphenylphosphine ligand.

The monohydride (III), on the contrary, derives from a  $d^8$  tetra-coordinated low spin iridium(I) atom, which is considered to give square planar coordination. Its electric moment of about 6,3 D shows that it is the cis isomer.

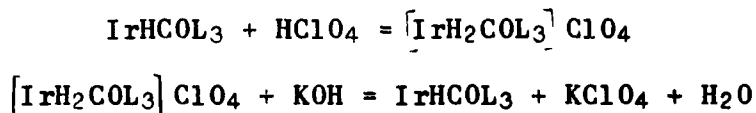
Another carbonylhydride belonging to these series, more stable and easier to prepare than both (II) and (III) is the hydridocarbonyl-tristriphenylphosphineiridium  $\text{IrHCOI}_3$  (IV). This can be obtained from any inorganic iridium carbonyl derivative as  $\text{K}_2[\text{IrCOBr}_5]$ ,  $\text{K}[\text{IrCOI}_5]$ ,  $\text{Ir}(\text{CO})_2\text{I}_3$  (4), by reduction with hydridoborate, in presence of an excess of triphenylphosphine, as well as by action of a mole triphenylphosphine on the hydrides (II) and (III). The elemental analysis of compound (IV) was indicative of the  $\text{IrI}_3$  group, the presence of a CO ligand was inferred from the IR spectrum and from the fact that (IV) could be obtained only using as starting material iridium carbonyl compounds. The number of hydridic hydrogen was deduced from the reaction with acids (see below) and confirmed by the IR spectrum.

The hydride (IV) is a yellow crystalline substance m.p.  $145^\circ$ , very

stable to air and moisture, soluble in benzene and chloroform, almost insoluble in ethanol. It shows two bands in IR region characteristic for Ir-H and CO stretching at 1920 and 2120  $\text{cm}^{-1}$ .

The carbonylhydride (IV) was also found in very little amount when  $[\text{IrH}_2\text{L}_3]\text{ClO}_4$  (1) was reacted with potassium hydroxide in ethanol solution. The main reaction is the hydrogenation of an unstable  $\text{IrHL}_3$  species at expenses of the  $\alpha$  hydrogen atoms of ethanol, which give acetaldehyde. Some of this acetaldehyde splitting in methane <sup>and</sup> carbon monoxide stabilizes the  $\text{IrHL}_3$  species giving  $\text{IrHCOL}_3$ .

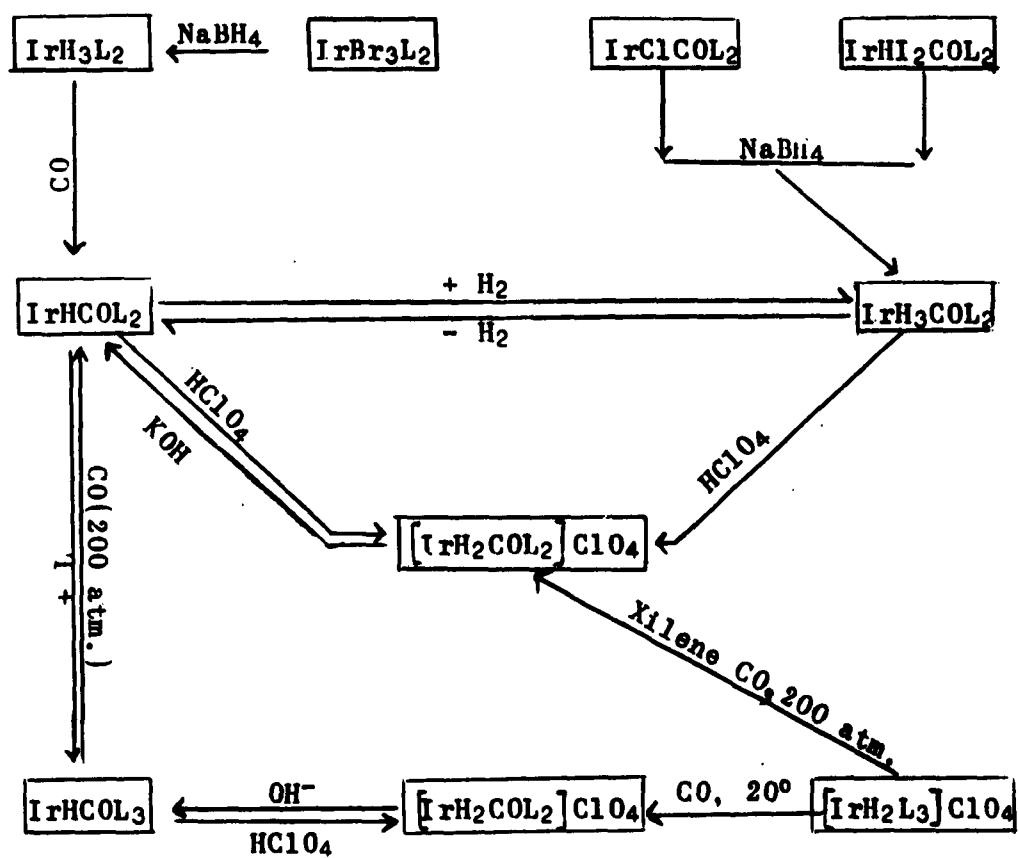
Compound (IV) as did compound (III) reacts reversibly with strong acids adding a proton. With perchloric acid the reaction is:

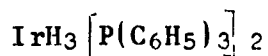


The perchlorate is a white crystalline substance, soluble in ethanol and benzene, which behaves in solution as a uni-univalent electrolyte. It shows in the IR three bands at 2155, 2118 and 2080  $\text{cm}^{-1}$  as expected. The cation  $[\text{IrH}_2\text{COL}_3]^+$  is coordinatively saturated and does not react in solution either with neutral or anionic ligands, and behaves also differently from the cation  $[\text{IrH}_2\text{COL}_2]^+$ , deriving from compound (II), which adds very easily halide ions and triphenylphosphine.

Its constitution was also confirmed by the preparation from  $[\text{IrH}_2\text{L}_3]^+\text{ClO}_4$  and carbon monoxide at ordinary temperature and pressure. The scheme on pag. 59 indicates the relationships among these new hydrido- and hydridocarbonyl compounds.

Relationships among hydrido and  
hydridocarbonyl(triphenylphosphine) compounds



EXPERIMENTAL

5 g  $\text{K}_3\text{IrBr}_6$  in 30 ml water were dropped in a solution of 7 g (4 moles) triphenylphosphine in 250 ml ethoxyethanol at  $80^\circ$ , and kept at this temperature for about two hours. The dark yellow precipitate, filtered and recrystallized from methylene chloride plus ethanol, was recognized from the IR spectrum and mixed m.p. as  $\text{IrHBr}_2 \left[ \text{P}(\text{C}_6\text{H}_5)_3 \right]_3$  (5). This compound (5,7 g) was dissolved in 200 ml methylene chloride and 3 eq of bromine solution (in  $\text{CCl}_4$ ) were added. The solution was evaporated to about 10 ml, precipitated with 100 ml ethanol and filtered. The yellow crystalline  $\text{IrBr}_3 \left[ \text{P}(\text{C}_6\text{H}_5)_3 \right]_2$  (5) was suspended in 200 ml ethanol and an ethanol solution of  $\text{NaBH}_4$  (about 1,5 g) was slowly added. The reduction was completed keeping the suspension for 1 hour at  $60-70^\circ$ . The white microcrystalline precipitate was filtered and washed with warm ethanol, benzene, methylene chloride, hot water, ethanol and hexane. Yield 2,5 g (72%) m.p.  $140-145^\circ$  (dec.) The compound could not be purified for its insolubility in all solvents.

The same compound could be obtained from 0,5 g  $\text{IrBr}_3 \left[ \text{P}(\text{C}_6\text{H}_5)_3 \right]_2$  in 30 ml tetrahydrofuran by reduction with  $\text{LiAlH}_4$  (0,15 g). After refluxing for about 15 minutes a few ml ethanol were added and then 100 ml 10%  $\text{KOH}$ . The filtered solution was washed with water, ethanol, methylene chloride.

The compound so prepared could not be obtained completely free from aluminum oxide; its IR spectrum was identical with that of the hydride prepared with  $\text{NaBH}_4$ , to say it had an intense band at  $1945 \text{ cm}^{-1}$  (IrH-stretching) and band at  $878 \text{ cm}^{-1}$  (IrH bending)

Found: C 58.4 ; H 5.57; Ir 26.5

for  $\text{C}_{36}\text{H}_{33}\text{IrP}_2$  calc: 59.9 ; 4.63; 26.8 .

When the reduction was carried out on 0,20 g  $\text{IrBr}_3 [\text{P}(\text{C}_6\text{H}_5)_3]_2$  with  $\text{LiAlD}_4$  instead of  $\text{LiAlH}_4$  and the decomposition made with  $\text{D}_2\text{O}$ , the corresponding deuterido  $\text{IrD}_3 \text{P}(\text{C}_6\text{H}_5)_3_2$  (0,19 g) was obtained. IR band at  $1360 \text{ cm}^{-1}$ .

Reaction with triphenylphosphine. 1 g of the hydride in 50 ml benzene were reacted with 0,5 g triphenylphosphine for a few minutes at  $60-70^\circ$ . On adding ethanol the known compound  $\text{IrH}_3 [\text{P}(\text{C}_6\text{H}_5)_3]_3$  (1), was obtained which was recognized by the IR spectrum

Found: C 66.7 ; H 4.5 ; Ir 20.1 ; P 10.1

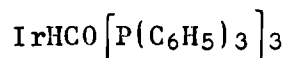
for  $\text{C}_{54}\text{H}_{48}\text{IrP}_3$  calc: 66.0 ; 4.9 ; 19.7 ; 9.4 .

Reaction with carbon monoxide. 1 g of the hydride was suspended in 40 ml benzene and CO was bubbled in for 1 hour until a clear solution was obtained. This was evaporated to 5 ml and ethanol was added. A yellow crystalline compound separated, m.p.  $132^\circ$ , which from IR spectrum and mixed m.p. was found identical to  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  (see below).

Reaction with pyridine. 0,55 g of the hydride were reacted at 60° with 10 ml pyridine and the solution was evaporated under vacuum. The residue, washed with methanol, was crystallized from benzene (10 ml) plus ethanol (20 ml). White crystals of  $\text{IrH}_3\text{C}_5\text{H}_5\text{N}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  (0,304 g) m.p. 134°. IR bands at 1700 and 2120  $\text{cm}^{-1}$ .

Found: C 61.38; H 4.90; N 1.80

for  $\text{C}_4\text{H}_3\text{8IrNP}_2$  calc: 61.8 ; 4.8 ; 1.75.



a) An ethanolic solution of 5,4 g  $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$  (3) was reacted with excess triphenylphosphine (7,1 g) at 70°, and then, drop by drop, with an ethanol solution of  $\text{NaBH}_4$  (1,5 g). The solution was then refluxed for 1 hour on w.b. and filtered. Light yellow needles (3,5 g), m.p. 187-188°, soluble in benzene, chloroform, insoluble in hexane and cold ethanol.

b) 2,5 g of  $\text{IrClCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  (3) in 30 ml tetrahydrofuran and 1,7g triphenylphosphine were reacted drop by drop with an ethanol solution of  $\text{NaBH}_4$  (0,7 g). The solution was refluxed for about 1 hour and evaporated under vacuum. The residue was recrystallized from benzene plus ethanol (2,1 g) m.p. 186-187°.

c) A very little amount of the same compound (1 mg) was obtained when an ethanol solution of  $\text{IrH}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{ClO}_4$  (1 g) (1) was reacted with KOH in ethanol. From the main product, formed by a mixture of the two isomeric  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3$ , the carbonyl compound was separated by

extraction with boiling ethanol and recognized from the IR spectrum and mixed m.p.

d) 0,180 g  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  (see below) in 20 ml benzene, were reacted with 0,12 g triphenylphosphine. The solution was refluxed for a few minutes, evaporated to 5 ml, and 25 ml ethanol were added. Yellow crystals (0,016 g) recognized as above.

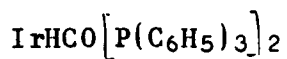
e) The same reaction was obtained using as starting materials  $\text{IrH}_3\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  described below.

Found a): C 65.3 ; H 4.96; Ir 19.4

b): 65.1 ; 4.83; 19.2

for  $\text{C}_{55}\text{H}_{46}\text{IrOP}_3$  calc: 66.0 ; 4.70; 19.05.

Mol. weight osmometric, in 1% benzene solution at 37°: Found 1015, calc. 1008.



a) The preparation of this substance from  $\text{IrH}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$  has been reported above.

b) 1,9 g of  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_3$  suspended in 5 ml xylene were reacted at 70° and 200 atm with CO per 15 h. The product was recrystallized from benzene plus hexane (1,2 g).

c) An ethanol solution of 0,3 g  $\text{IrH}_2\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{ClO}_4$  was neutralized with ethanolic potassium hydroxide. The yellow precipitated was washed with water and recrystallized from benzene plus hexane (0,12 g). The products obtained as described in a) b) c) were recognized identical from the IR spectrum and mixed m.p.

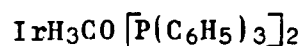
Light yellow crystals soluble in benzene, chloroform, tetrahydrofuran, very little soluble in alcohols and hydrocarbons.

Found b): C 58.59; H 4.20; Ir 26.00

c): 59.1 ; 4.25; 25.94

for  $C_{37}H_{31}IrOP_2$  calc: 59.5 ; 4.12; 25.82.

Mol. weight osmometric, in 2% chloroform at 37°: Found 720, calc. 746.



a) A solution of 6,7 g  $K_2 [Ir(CO)_2I_5]$  (4) in 100 ml ethanol, was refluxed with 4,4 g triphenylphosphine for 1 hour. After cooling the solution, the yellow crude precipitate of  $IrHI_2CO [P(C_6H_5)_3]_2$  was filtered and recrystallized from benzene plus hexane, (2,8 g) m.p. 155°. Soluble in benzene, chloroform, tetrahydrofuran, insoluble in alcohols and hydrocarbons.

Found: C 44.75; H 3.24; I 24.2 ; Ir 19.5

for  $C_{37}H_{31}I_2IrOP_2$  calc: 44.0 ; 3.13; 25.4 ; 19.3

IR spectrum bands at 2040 and 2180  $cm^{-1}$  (Ir-H and CO stretching region).

b) 0,5 g of the above compound in 20 ml benzene were reacted at 60-70°, drop by drop, with a saturated ethanol solution of  $NaBH_4$  (0,2 g). The solution was then refluxed for about 1 hour and precipitated with 50 ml ethanol. Ivory-white crystals (0,2 g) m.p. 146°, soluble in benzene, chloroform, tetrahydrofuran, insoluble in alcohols and hydrocarbons showing in the IR spectrum 3 intense bands at 1785, 1965 and 2080  $cm^{-1}$ . When this compound was recrystallized it showed new

IR bands at 1960 and 2000  $\text{cm}^{-1}$ .

A specimen of about 0,1 g which was recrystallized after having been left to air for two weeks was recognized from its IR spectrum identical with the monohydride  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , previously described.

b) 0,5 g  $\text{IrClCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  (3) in 30 ml tetrahydrofuran were reacted with 0,1 g  $\text{LiAlH}_4$ . After refluxed for about one hour a few drop ethanol were added to decompose the excess  $\text{LiAlH}_4$  and the solution evaporated under vacuum, extracted with benzene (20 ml) and precipitated with hexane (30 ml).

By the same method, but using  $\text{LiAlD}_4$  for the reduction and  $\text{D}_2\text{O}$  for the decomposition the corresponding deuteride  $\text{IrD}_3\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  was prepared, showing IR bands at 1278-1510 and 1980  $\text{cm}^{-1}$ .

c) The same product was obtained when hydrogen was bubbled in a solution of 0,2 g  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  in 25 ml benzene for about 2 hours and the solution precipitated with hexane.

Found a): C 59.62; H 4.50; Ir 26.20

b): 59.00; 4.50; 26.30

for  $\text{C}_{37}\text{H}_{33}\text{IrOP}_2$  calc: 59.50; 4.45; 25.78.



a) 2,6 g  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_2]_3$  suspended in 40 ml ethanol were reacted with 5 ml of an ethanol solution of 4%  $\text{HClO}_4$  gently warming until complete dissolution took place. The yellow solution was filtered and precipitated adding water drop by drop. Creme-white crystals

(1,8 g) m.p. 137° soluble in benzene, ethanol and tetrahydrofuran.

IR bands: 2011, 2118 and 2155  $\text{cm}^{-1}$ .

When the crystallization took place very slowly from aqueous ethanol an isomeric form m.p. 210-211° separated.

IR bands: 2011, 2118 and 2185  $\text{cm}^{-1}$ .

The low melting isomer could be transformed in the high melting by recrystallization from hot aqueous ethanol.

The low melting isomer, after melting at 137° solidified and melted once more at 210-220°.

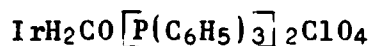
b) 1 g  $\text{IrH}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{ClO}_4$  (1) was reacted with carbon monoxide at 25° and 150 atm. The product was washed with benzene and recrystallized from hot ethanol.

Found a): C 59.39; H 4.22; Cl 3.25; Ir 18.05

b): 59.45; 4.42; 3.20; 17.90

for  $\text{C}_{55}\text{H}_{47}\text{ClIrO}_5\text{P}_3$  calc: 60.6 ; 4.27; 3.20; 17.32.

Electric conductivity in  $10^{-3}\text{M}$  acetone  $\Lambda = 130 \text{ ohm}^{-1}\text{cm}^2$ .



a) 1 g  $\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  were reacted at 60° with a solution containing 0,7 g  $\text{HClO}_4$  in 50 ml ethanol, until complete solution took place. After concentration in vacuo to about 20 ml, on cooling yellow rhombohedral crystals separated (0,85 g) soluble in chloroform, benzene, acetone and hot ethanol, m.p. 103°.

b) The same reaction was observed using as starting material  $\text{IrH}_3\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  but in this case the reaction gave place to evolution of hydrogen.

Found: C 52.28; H 3.65.

for  $\text{C}_{37}\text{H}_{32}\text{ClIrO}_5\text{P}_2$  calc: 52.50; 3.81.

IR band at 2050, 2085 and 2165  $\text{cm}^{-1}$ .

Electric conductivity in  $10^{-3}\text{M}$  acetone at  $30^\circ$   $\Lambda = 1,33 \text{ ohm}^{-1}\text{cm}^2$ .

#### References

- (1) M. Angoletta, Gazz. Chim. It. 92, 811 (1962).
- (2) J. Chatt, unpublished work
- (3) L. Vaska, J.W. Diluzio, J. Chem. Am. Soc. 83, 2784, (1961)
- (4) L. Malatesta, L. Naldini, J. Chem. Soc. (in press)
- (5) M. Angoletta, A. Araneo, Gazz. Chim. It. 1963 (in press).

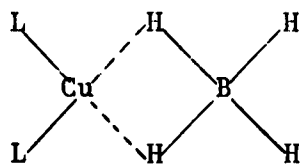
Part VI.a) "Bis(triphenylphosphine)copper(I)hydridoborate"

preliminary report

by

L. Naldini and F. Cariati

When complexe triphenylphosphinecopper(I) compounds  $LCuX$ ,  $L_2CuY$ ,  $L_3CuX$ , (where  $X = Cl, I$ ;  $Y = I$ ;  $L = P(C_6H_5)_3$ ), were treated with sodium hydridoborate, a stable compound  $CuL_2BH_4$  was obtained. This was a white, crystalline, diamagnetic, not salt-like substance. In the IR spectrum, two different H-stretching types of bands were observed which were assigned to terminal hydrogen stretching (B-H) and to bridging hydrogen stretching Cu-H-B, resp. On this hypothesis the substance would be an electron deficient molecule, with two three-centre bonds, such as:



and its structure could be symbolized as two tetrahedra having copper and boron atom in their respective centres joined through a hedge. Such a structure, having a  $C_{2v}$  symmetry would in fact give place to the two observed double hydrogen stretching bands.

Part VI.

b) "Monohalogenotetrakis(triphenylphosphine)pentagold."

preliminary report

by

L. Malatesta, L. Naldini, F. Cariati and G. Simonetta

When the triphenylphosphinegold(I) compounds  $\text{LAuCl}$  and  $\text{L}_2\text{AuI}$  were reacted with sodium hydridoborate they gave place to compounds which were different than those obtained from the corresponding  $\text{Cu(I)}$  compounds described above. The reactions gave in fact place to red, crystalline, diamagnetic compound which behaved as a strong electrolyte and had a composition corresponding to  $\text{Au}_5\text{ClL}_4$  and  $\text{Au}_5\text{IL}_4$  resp.

Work on this unusual and interesting compound is in progress; at present it can only be stated that the chlorine is anionic and that it can be exchanged with other anions.

III) Trihydrido-trisphenylphosphineiridium,  $I_3H_3L_3$  prepared in two isomers (M. Angoletta).

IV) Reaction products of  $IrH_3L_3$  with halogens, acids, oxo-acids described. (M. Angoletta, A. Araneo).

V) Trihydridobis(trisphenylphosphineiridium  $IrH_3L_3$ , prepared. Three iridium carbonylhydrides  $IrHCOL_3$ ,  $IrHCOL_2$ ,  $IrH_3COL_2$  prepared and their reactions and mutual relationships studied. (L. Malatesta, M. Angoletta and G. Caglio).

VI) Preliminary report on a copper complex hydrido-borate  $CuL_2BH_4$  (L. Naldini and F. Cariati) and on a zero-valent complex gold compound  $Au_3L_4Cl$ . (L. Malatesta, L. Naldini, F. Cariati and G. Simonetta).

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II) Two new rhenium hydrides with triphenylphosphine (L) prepared:  $\text{ReH}_5\text{L}_3$  fully characterized and a compound  $\text{ReH}_5\text{-}\gamma\text{-L}_2$  still uncertain as for the hydrogen content. (L. Malatesta, M. Freni and V. Valentini).

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ERRATA CORRIGE

Page 18, line 12 : for " (I) " read " (II) "

Page 21, line 16 : for " (I) " read " (II) "

Page 32, line 21: for "estimates as 3,3 - 3,4 D,"  
read "estimates as 4,3 - 4,4 D "

Page 42, line 19:

for " $\text{IrH}_2\text{Cl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3 \cdot \text{C}_6\text{H}_4$ " read " $\text{IrHCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3 \cdot \text{C}_6\text{H}_5$ "

Page 43, line 4: for " $\text{C}_6\text{OHS}_3\text{Cl}_2\text{IrP}_3$ " read " $\text{C}_6\text{OHS}_2\text{Cl}_2\text{IrP}_3$ "

Page 59, bottom line of the scheme:

for " $[\text{IrH}_2\text{COL}_2] \text{ClO}_4$ " read " $[\text{IrHCOL}_3] \text{ClO}_4$ "

Page 61, line 9: for " $\text{IrD}_3\text{P}(\text{C}_6\text{H}_5)_3 \cdot 2$ " read " $\text{IrD}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ "

Page 66, line 9: for "210-220°" read "210-211°"