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Hydridochlorobis(triphenylphosphine)platinum(II) and Some Related Compounds[1]

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In the course of studies on the hydrogenation of soy bean oil methyl ester in the presence of soluble catalysts, we have investigated the properties of hydridochlorobis(triphenylphosphine)platinum(II) and some related compounds. The hydridochloro complex was obtained in both *cis* and *trans* forms, and methods of interconverting these have been developed. A by-product of the formation of the hydridochloro complex is the hydroxochloro complex. The *cis* and *trans* forms of the hydridochloro complex, as well as the hydroxochloro complex, form 1:1 adducts with tin(II) chloride. These substances, which probably contain tin–platinum bonds, have remarkable catalytic properties.

Introduction

In recent years there has been considerable interest in soluble hydrogenation catalysts, and several metal ions and complexes have been found to be effective in the hydrogenation of unsaturated compounds. For example, hydrogenations catalyzed by pentacyanocobaltate ion,[2] ruthenium(II) ion,[3] metal carbonyls,[4] Ziegler-type catalysts,[5] and mixtures of platinum(II) compounds with tin(II) chloride[6] have been reported. Moreover, it has been observed that hydrido–transition metal complexes activate molecular hydrogen, supposedly through electron occupation of the vacant d orbitals of the metal ion.[7] The reduced pentacyanocobalt complex has been formulated as a hydrido ion,[8] and the isolation of hydrido complexes of platinum[9] and osmium[10] has been reported also.

In the course of studies on the hydrogenation of soy bean oil methyl ester in the presence of soluble catalysts, we have investigated the properties of hydridochlorobis(triphenylphosphine)platinum(II) and some related compounds. Since these complexes present some unusual features, a brief report on them is appropriate.

All of these substances have the remarkable property of catalyzing the hydrogenation of some, but not all, of the double bonds in long-chain unsaturated esters. In each case, one double bond remains largely unattacked. That the ability to catalyze hydrogenation is effected through transfer of the hydrogen of the hydride complex to the hydrocarbon chain is suggested by the isolation of an isoprene–platinum complex. The catalytic action of these complexes will be described in detail elsewhere.

Experimental

(1) ***cis*-Dichlorobis(triphenylphosphine)platinum(II), $[PtCl_2(P(C_6H_5)_3)_2]$**, was prepared by the method described in the literature.[11] A solution of 4 g. of potassium tetrachloroplatinate(II) in 50 ml. of water was added dropwise, with stirring, to a boiling solution of 5 g. of triphenylphosphine in 60 ml. of ethanol. White crystals separated immediately. The mixture was stirred at 60° for 2 hr., after which the crystals were filtered off and washed successively with hot water, hot ethanol, and ether; yield 6.26 g. (80%). The crystals were purified by dissolving them in chloroform and reprecipitating with *n*-heptane; m.p. 310–312° dec. Grinberg and Razumova report 308° dec.

(2) ***trans*-Hydridochlorobis(triphenylphosphine)platinum(II), *trans*-$[PtHCl(P(C_6H_5)_3)_2]$**, has been prepared by Chatt and Shaw.[12] Their method has been improved as follows: 2 g. of dichlorobis(triphenylphosphine)platinum(II) was dissolved, at room temperature, in 50 ml. of ethanol containing 1.26 g. of hydrazine hydrate. After the solution was refluxed on a steam bath for 5 min., 1.20 g. of acetic acid, 20 ml. of water, and 10 ml. of ethanol were added. Upon cooling, colorless crystals separated. These were filtered and washed with methanol; yield 1.32 g. of colorless prisms; m.p. 210–215° dec., as Chatt and Shaw reported. After recrystallization from a 1:2 mixture of benzene and methanol, the melting point was 213–215° dec.

Anal. Calcd. for $C_{36}H_{31}ClP_2Pt \cdot CH_3OH$: C, 56.37; H, 4.47. Found: C, 56.79; H, 4.48.

The material was dried over phosphorus(V) oxide at 100° under diminished pressure (4 mm.) for 6 hr. to remove the methanol. The compound then showed m.p. 210–214° dec. The strong band at 2220 cm.$^{-1}$ in the infrared spectrum in HCBD mull is shown in curve 1, Figure 1.

Anal. Calcd. for $C_{36}H_{31}ClP_2Pt$: C, 57.17; H, 4.13; Cl, 4.68. Found: C, 57.12; H, 4.29; Cl, 4.77.

The filtrate from the original preparation was concentrated to one-third of its volume, 10 ml. of water was added, and the mixture was cooled; 0.5 g. of yellow powder separated and was filtered and washed with water. This compound melted at 118–124° and was shown by analysis and from the infrared spectrum to be hydroxochlorobis(triphenylphosphine)platinum(II), $[PtOHCl(P(C_6H_5)_3)_2]$ (expt. 8).

(3) **Effect of Varying the Temperature in the Formation of *trans*-$[PtHCl(P(C_6H_5)_3)_2]$. The *cis* Isomer.**—It was observed

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[1] A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by the Northern Utilization Research and Development Division of the Agricultural Research Service.

[2] See, for example, M. Iguchi, *J. Chem. Soc. Japan*, **63**, 634 (1942); J. Kwiatek, I. L. Mador, and J. K. Seyler, "Reactions of Coordinated Ligands and Homogeneous Catalysis," Advances in Chemistry Series, No 37, American Chemical Society, Washington, D. C., 1963, p. 201; A. F. Mabrouk H. J. Dutton, and J. C. Cowan, *J. Am. Oil Chemists Soc.*, **41**, 153 (1964).

[3] J. Halpern, J. F. Harrod, and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961).

[4] E. N. Frankel, H. M. Peters, E. P. Jones, and H. J. Dutton, *J. Am. Oil Chemists Soc.*, **41**, 186 (1964); E. N. Frankel, E. P. Jones, and C. A. Glass, *ibid.*, **41**, 392 (1964).

[5] M F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Am. Chem. Soc.*, **85**, 4014 (1963).

[6] R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963).

[7] J. Halpern, *Quart. Rev.* (London), **10**, 463 (1956).

[8] See, for example, K. K. King and M. E. Winfield, *J. Am. Chem. Soc.*, **83**, 3366 (1961).

[9] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

[10] L. Vaska, *J. Am. Chem. Soc.*, **86**, 1943 (1964).

[11] K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 242 (1936); A. A. Grinberg and Z. A. Razumova, *Zh. Prikl. Khim.*, **27**, 105 (1954).

[12] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5082 (1962).

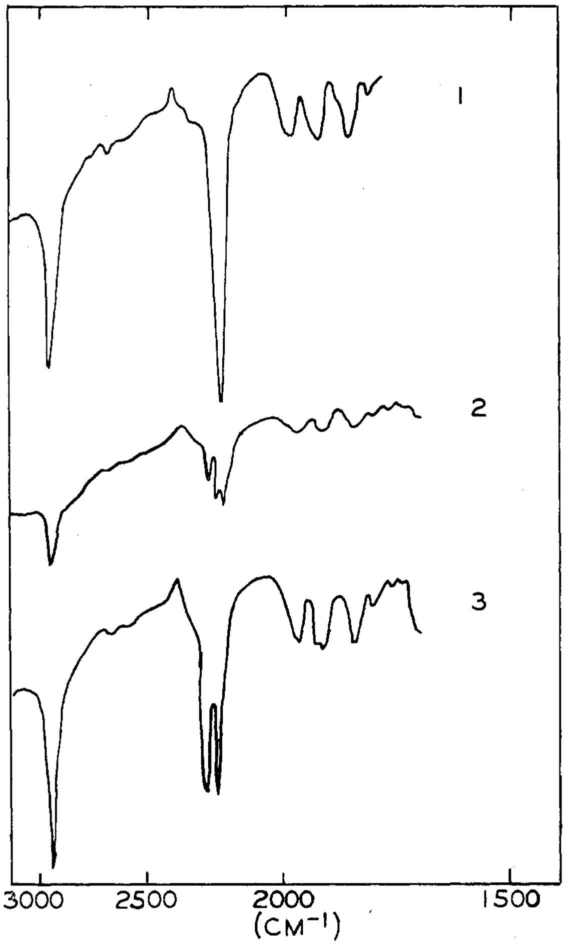


Figure 1.—Infrared spectra: 1, *trans*-[Pt(P(C_6H_5)$_3$)$_2$HCl]; 2, mixture of *cis*- and *trans*-[Pt(P(C_6H_5)$_3$)$_2$HCl]; 3, *cis*-[Pt(P(C_6H_5)$_3$)$_2$HCl].

that, when expt. 2 was repeated, but with heating of the solution to 60° for 5 min. instead of boiling it, a mixture of the *cis* and *trans* isomers of [PtHCl(P(C_6H_5)$_3$)$_2$] was obtained (curve 2, Figure 1). The mixture of *cis*- and *trans*-hydrido complexes was recrystallized from benzene and ethyl ether at room temperature. The first fraction was the *cis* hydride, which separated as scaly crystals. The second fraction was the *trans* hydride.

(4) ***cis*-Hydridochlorobis(triphenylphosphine)platinum(II), [PtHCl(P(C_6H_5)$_3$)$_2$].**—One gram of *cis*-[PtCl$_2$(P(C_6H_5)$_3$)$_2$] was dissolved in a mixture of 40 ml. of methanol and 40 ml. of ethyl ether containing 0.63 g. of hydrazine hydrate. The mixture was refluxed on a steam bath for 15 min., and then 0.45 g. of acetic acid and 30 ml. of water were added to it. On cooling, crystals separated; these were washed with methanol, giving 0.45 g. of colorless, scaly crystals, which were recrystallized from benzene and ethyl ether at room temperature; m.p. 215–220 dec.; ν (HCBD mull), 2260 and 2225 cm.$^{-1}$ (curve 3, Figure 1).

Anal. Calcd. for $C_{36}H_{31}ClP_2Pt \cdot C_6H_5$: C, 60.46; H, 4.46. Found: C, 59.87; H, 4.70.

The *cis*-hydrido complex benzene adduct was dried at 100° under a pressure of 4 mm. for 6 hr.; m.p. 215–218° dec.

Anal. Calcd. for $C_{36}H_{31}ClP_2Pt$: C, 57.17; H, 4.13. Found: C, 57.06; H, 4.35.

To the original filtrate was added 40 ml. of water. When the mixture was cooled in an ice bath, an additional 0.11 g. of *cis*-hydrido complex separated. When the filtrate was concentrated on a steam bath under diminished pressure, 0.35 g. of yellow powder separated. This was filtered and washed with water and proved to be hydroxochlorobis(triphenylphosphine)platinum(II), which melted at 118–122°.

(5) ***cis–trans* Isomerization of the Hydrido Complex.**—*cis*-[PtHCl(P(C_6H_5)$_3$)$_2$]·C_6H_6 was recrystallized after refluxing in benzene and ethyl ether to give *trans*-[PtHCl(P(C_6H_5)$_3$)$_2$]·C_6H_6; m.p. 210–214° dec.

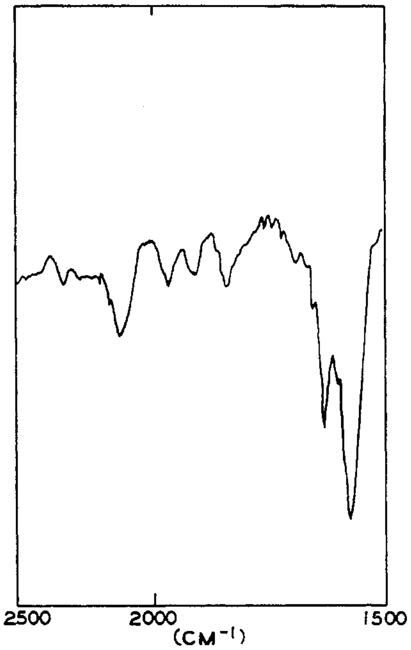


Figure 2.—Infrared spectrum of the tin adduct of [Pt(P(C_6H_5)$_3$)$_2$-HCl].

Anal. Calcd. for $C_{36}H_{31}ClP_2Pt \cdot C_6H_6$: C, 60.46; H, 4.46. Found: C, 60.69; H, 4.61.

The benzene in these crystals was lost when the material was dried at 100° at a pressure of 4 mm.

Anal. Calcd. for $C_{36}H_{31}ClP_2Pt$: C, 57.17; H, 4.13. Found: C, 57.36; H, 4.03.

Recrystallization of the *cis*-hydrido complex from benzene and methanol converted it to the *trans* complex, but recrystallization from ethanol did not; 0.25 g. of *cis*-hydrido complex was recrystallized from 50 ml. of absolute ethanol and washed with methanol. The 0.195 g. of pure *cis*-hydrido complex obtained was dried over P_4O_{10} at 100° under diminished pressure. This compound shows a spectrum identical with that of the starting material (curve 3, Figure 1).

Anal. Calcd. for $C_{36}H_{31}ClP_2Pt$: C, 57.17; H, 4.13. Found: C, 57.59; H, 4.42.

(6) **Preparation of the Tin(II) Adduct of [PtHCl(P(C_6H_5)$_3$)$_2$].**—A solution of 1 g. of *trans*-[PtHCl(P(C_6H_5)$_3$)$_2$] and 2 g. of $SnCl_2 \cdot 2H_2O$ in 120 ml. of ethanol was refluxed on a steam bath for 30 min. The solution was filtered and allowed to stand at room temperature, whereupon 0.85 g. of a yellow-orange powder separated. This was washed with ether, dissolved in acetone, and precipitated by adding a mixture of equal amounts of ether and *n*-heptane. It was dried over P_4O_{10} at 100°, under reduced pressure; m.p. 172–173°; ν (HCBD mull), 2100 cm.$^{-1}$ (Figure 2).

Anal. Calcd. for $C_{36}H_{31}Cl_3P_2SnPt$: C, 45.61; H, 3.30; Cl, 11.24. Found: C, 44.12; H, 3.39; Cl, 11.40.

What was apparently the same product was obtained when *cis*-[PtHCl(P(C_6H_5)$_3$)$_2$] was substituted for the *trans* isomer; m.p. 165–170°; ν (HCBD mull), 2100 cm.$^{-1}$.

Anal. Found: C, 44.34; H, 3.30; Cl, 11.17.

(7) **The isomerization of the hydridochloro complex** from the *trans* form to the *cis* form was accomplished by refluxing a solution of 0.11 g. of *trans*-[PtHCl(P(C_6H_5)$_3$)$_2$] and 0.033 g. of $SnCl_2 \cdot 2H_2O$ in 20 ml. of ethanol for 30 min. The white crystals which formed upon cooling were filtered and washed with ether; yield, 0.065 g. of *cis*-[PtHCl(P(C_6H_5)$_3$)$_2$]; m.p. 217–224°, ν (HCBD mull), 2225 and 2260 cm.$^{-1}$. From the filtrate, an additional 0.04 g. of the *cis*-hydrido complex was recovered. The infrared spectrum of both fractions was virtually identical with that shown in curve 3, Figure 1.

(8) When an excess of hydrazine is used in the preparation of the hydrido complex, its basic action brings about a partial hydrolysis of the dichloro complex, with the formation of a hydroxochloro complex. Hydroxochlorobis(triphenylphosphine)platinum(II), [$PtOHCl(P(C_6H_5)_3)_2$] was prepared as follows: a solution of 1 g. of *cis*-dichlorobis(triphenylphosphine)-platinum(II) and 0.7 ml. of hydrazine hydrate in 20 ml. of ethanol and 10 ml. of water was refluxed for 30 min. After neutralization with acetic acid and addition of 40 ml. of water, the yellow powder which separated upon cooling was washed with water and purified by dissolving in 20 ml. of benzene and reprecipitating by the addition of 100 ml. of *n*-heptane, giving 0.6 g. of complex; m.p. 118–121°. The infrared spectrum showed the characteristic OH absorption bands at 1660, 1360, 1120, and 720 cm.$^{-1}$ in HCBD mull. The material was dried over P_4O_{10} at 100° under vacuum.

Anal. Calcd. for $C_{36}H_{31}OClP_2Pt$: C, 55.99; H, 4.04. Found: C, 55.74; H, 3.96.

(9) The tin(II) chloride adduct of hydroxochlorobis(triphenylphosphine)platinum(II) was obtained by refluxing a solution of 0.4 g. of hydroxochlorobis(triphenylphosphine)platinum-(II) and 0.4 g. of $SnCl_2 \cdot 2H_2O$ in a mixture of 15 ml. of acetone and 30 ml. of ethanol for 30 min. and then concentrating the solution under diminished pressure. On cooling, a yellow powder formed. This was filtered and washed with ether; m.p. 165–170°.

Anal. Calcd. for $C_{36}H_{31}OCl_3P_2SnPt \cdot 3H_2O$: C, 42.56; H, 3.67; Cl, 10.47. Found: C, 41.93; H, 3.38; Cl, 10.11.

(10) **Isopropenylchlorobis(triphenylphosphine)platinum(II), [$PtC_5H_9Cl(P(C_6H_5)_3)_2$]**, was prepared from the dichloro complex as follows: a solution of 0.5 g. of *cis*-[$PtCl_2(P(C_6H_5)_3)_2$], 1.08 g. of $SnCl_2 \cdot 2H_2O$, and 4 0 g. of isoprene in a mixture of 30 ml. of methanol and 30 ml. of benzene was vibrated in an autoclave under 550 p.s.i. of hydrogen at 60° for 3 hr. The yellow solution was evaporated to dryness on a steam bath under diminished pressure, and the solid residue was extracted with ethyl ether. The yellow powder which remained was dissolved in a little methanol and benzene. This solution was developed in a chromatographic column (diameter 2.5 cm.) containing 50 ml. of alumina and then eluted with benzene, with ether, and with methanol, in turn. The solution eluted with methanol was evaporated under diminished pressure and the residue was extracted with ether. This left a pale yellow powder. The infrared spectrum of this material showed bands at 2950, 2920, 2840, 1730, 1380, 1120, and 725 cm.$^{-1}$ and is quite different from that of [$PtCl_2(P(C_6H_5)_3)_2$]. Analysis showed this material to be quite impure, and all attempts to purify it were unsuccessful.

Anal. Calcd. for $C_{41}H_{39}ClP_2Pt$: C, 58.78; H, 5.06; Cl, 4.12. Found: C, 57.84; H, 5.01; Cl, 5.13.

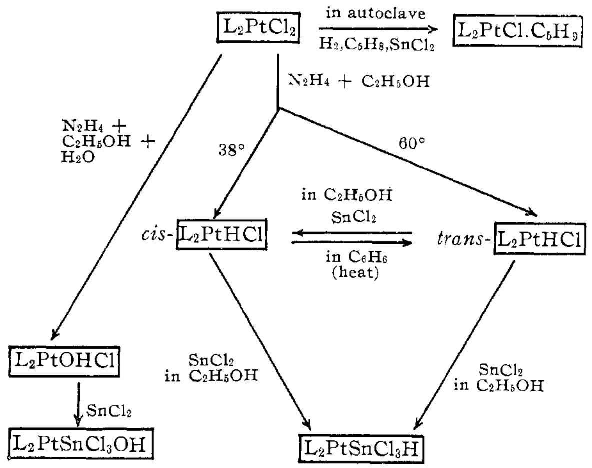
The low value for carbon and the high value for chlorine suggest that some of the tin chloride adduct is still present. The calculated values for a mixture containing 97% of the isoprenyl compound and 3% of the tin(II) chloride dihydrate are C, 57.59; H, 4.69; Cl, 5.11, in good agreement with the values found.

Results and Discussion

The experimental results are summarized in Chart I. Chatt and Shaw[12] reported that the hydrogen atom has a high *trans* effect in platinum complexes, and only the *trans*-hydridoplatinum(II) complex was isolated in their experiments. However, we have found that if the preparation is carried out at a low temperature, *cis*-hydridochlorobis(triphenylphosphine)platinum(II) can also be isolated.

Chart I

The Preparation of Some Complexes Related to [$Pt((C_6H_5)_3P)_2Cl_2$]



According to Chatt, the hydrogen atom exerts a very strong ligand field effect and is more hydridic than acidic in character. The halogen atom in the *trans* position to the hydrogen atom is, therefore, more anionic than is usual in platinum(II) complexes. On this account, the *cis*-hydrido complex may accept electrons from benzene and thus change to the more stable *trans*-hydrido complex.

When either the *cis*- or *trans*-hydridochloro complex was allowed to react with tin(II) chloride in ethanol, a yellow-orange product was obtained. This contains tin and platinum in a 1:1 ratio. The infrared absorption band assigned to the platinum–hydrogen stretching in this compound is shifted to 2100 cm.$^{-1}$ (Figure 2). It is probable that this compound contains a tin–platinum bond, as been shown to be the case in analogous complexes,[13] and that the shift of electrons from the tin toward the platinum allows the hydrido group to become more ionic. This would explain its increased catalytic power in the hydrogenation of unsaturated compounds.

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(13) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).