Homogeneous Catalysis in the Reactions of Olefinic Substances.[1a] VI. Selective Hydrogenation of Methyl Linoleate and Isomerization of Methyl Oleate by Homogeneous Catalysis with Platinum Complexes Containing Triphenylphosphine, -arsine, or -stibine[1b]

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Abstract: A series of complexes of the type $(R_3Q)_2MX_2$ (R = alkyl or aryl; Q = P, As, or Sb; M = Ni, Pd, or Pt; X = a halogen or pseudohalogen) has been found to have unusual catalytic properties. In the cases of the Pt and Pd complexes, these properties are greatly enhanced by the addition of $M'X_2$ or $M'X_4$ (M' = Si, Ge, Sn, or Pb). The resulting complexes have the ability to catalyze the hydrogenation of methyl linoleate to the monoene stage, but no further. The hydrogenation is preceded by conversion of *cis* double bonds to *trans*, and by migration of the double bonds along the hydrocarbon chain to give a conjugated system. The hydrogenation is best brought about by elemental hydrogen, but it can be effected by methanol in the absence of hydrogen.

The discovery and isolation of transition metal complexes containing the hydrido ligand opened up several new areas of coordination chemistry, not the least of which is the study of their relationship to catalytic hydrogenation. The catalytic activity is connected with the presence of low-lying unfilled orbitals on the metal (especially those with a high degree of d character) which can form weak bonds with the hydride ion by accepting electrons from it. The character of these bonds, and hence the catalytic activity of the complexes, is greatly modified by the nature of the other ligands in the complex. As Halpern pointed out,[2] the large activation barriers which reflect the high dissociation energy of the hydrogen molecule (about 103 kcal/mole) can be partially overcome by the use of suitable hydrido–transition metal complexes as catalysts. Many studies on homogeneous hydrogenations under the influence of these catalysts have been reported.[3] Recently, hydride complexes of the transition metals have been extensively investigated,[4] and some correlation between the configurations of hydride complexes and the processes of hydrogenation have been proposed.[5]

For the past 2.5 years, we have been studying the isomerization and selective hydrogenation of the esters of long-chain unsaturated esters, particularly those contained in soybean oil.[6] More recently, the study has been extended to other types of polyunsaturated compounds, and it has been observed that the reactions reported in this paper are not confined to the unsaturated esters.

For the most part, the catalysts which have been used are of the type $(R_3Q)_2MX_2$, where R represents an alkyl or aryl group, Q represents phosphorus, arsenic, or antimony, M represents platinum, palladium, or nickel, and X represents a halogen or halogenoid. In most cases, a compound of the type $M'X_2$ or $M'X_4$ (M' represents silicon, germanium, tin, or lead) has been added, converting one (or perhaps more) of the X ligands in the hard metal complex to a $-M'X_3$ or similar ligand. The interesting colored complexes of tin chloride with platinum metals have been known for a decade,[7] and some of these systems have been found to catalyze hydrogenation.[8]

This paper is devoted mainly to a description of the preparation and catalytic properties of the platinum compounds but will serve also as a general introduction to other aspects of the subject. These will be described in later reports. Originally, we were of the opinion that the presence of two metals in the complex is essential for the peculiar catalytic properties which were observed, but more recent studies have shown that this is not the case, the $-M'X_3$ group is simply an electrophilic ligand which modifies the M–H bond to such an extent that the complex can react with double bonds. In some cases, at least, the –CN group produces similar

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(1) Earlier articles in the series: part I, *Inorg. Chem.*, 4, 1618 (1965); part II, Proceedings of the Symposium on Coordination Compounds, Tihany, Hungary, 1964, p 67; part III, *J. Am. Oil Chemists Soc.*, 43, 337 (1966); part IV, Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press; part V, *J. Am. Oil Chemists Soc.*, in press. (b) 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) J. Halpern, *Advan. Catalysis*, 9, 324 (1954); 11, 301 (1958).

(3) See, for example, J. Kwaitek, 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); M. Murakami, J. W. Kang, H. Itatani, S. Senoh, and N. Matsusato, *Nippon Kagaku Zasshi*, 84, 48 (1963); J. Halpern, J. F. Harrod, and B. R. James, *J. Am. Chem. Soc.*, 83, 753 (1961); 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); M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Am. Chem. Soc.*, **85**, 4014 (1963); R. D. Gillard, J. A. Osborn, P. B. Stockwell, and G. Wilkinson, *Proc. Chem. Soc.*, 284 (1964); S. J. Lapporte and W. R. Schuett, *J. Org. Chem.*, 28, 1947 (1963); C. E. Castro and R. D. Stephens, *J. Am. Chem. Soc.*, 86, 4358 (1964); L. Vaska, *ibid.*, **87**, 4970 (1965).

(4) M. L. H. Green, *Advan. Inorg. Nucl. Chem.*, 6, 115 (1965); A. D. Ginsberg, "Transition Metal Chemistry," Vol. 1, Marcel Dekker Inc., New York, N. Y., 1965, Chapter 3.

(5) (a) L. Vaska, *Inorg. Nucl. Chem. Letters*, 1, 89 (1965); (b) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 131 (1965).

(6) Parts II and III in this series; see ref 1a.

(7) G. H. Ayres, *Anal. Chem.*, **25**, 1622 (1953); A. S. Meyer, Jr., and G. H. Ayres, *J. Am. Chem. Soc.*, 77, 2671 (1955); J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).

(8) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1692 (1963).

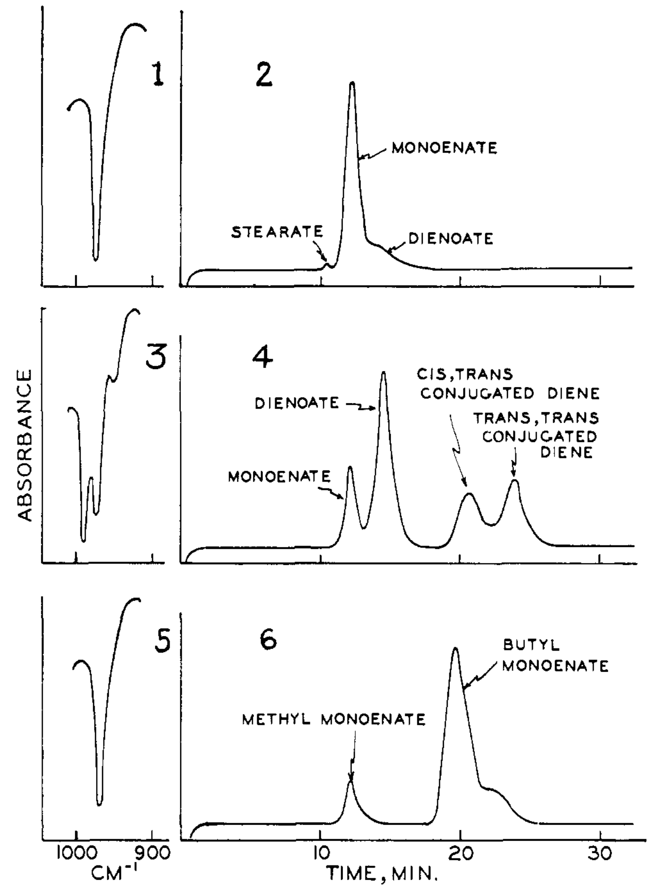
effects. Typical catalysts in the platinum series are (1) a mixture of tin(II) chloride and dichlorobis(triphenylarsine)platinum(II) and (2) a mixture of tin(II) chloride and dichlorobis(triphenylphosphine)platinum(II). These platinum complexes catalyze isomerization reactions as well as hydrogenation;[6] their effectiveness in a solvent mixture of methanol and benzene is the same under either nitrogen or hydrogen pressure. On the other hand, the nickel catalysts, such as diiodobis(triphenylphosphine)nickel(II), catalyze hydrogenation more than isomerization and cause no isomerization of oleate under nitrogen pressure.[9] Effective catalysts in the palladium series are (1) mixtures of tin(II) chloride and dichlorobis(triphenylphosphine)palladium(II) and (2) dicyanobis(triphenylphosphine)palladium(II).[10]

Hydrogenation, with all of the catalysts, usually has been carried out under high pressures of hydrogen or an inert atmosphere of nitrogen. However, when the reaction is carried out at atmospheric pressure (either nitrogen or hydrogen), the platinum[11] and palladium[10] catalysts effect isomerization and migration of double bonds but not hydrogenation.

The most interesting catalytic property which these compounds show is their ability, under suitable experimental conditions, to bring about the hydrogenation of *all but one* double bond in a compound containing two or more such bonds.[12] This is apparently effected by the more or less random migration of isolated double bonds to form conjugated dienes, which, under suitable conditions, are then hydrogenated selectively to monoenes.[13] Under other conditions, the formation of the conjugated system is not accompanied by hydrogenation.[11] The migration of double bonds is accompanied by their conversion from the *cis* to the *trans* form.[6,13]

A mixture of benzene and methanol is a good solvent for the reduction with platinum and palladium complexes, but not for reduction with nickel complexes because these are unstable in alcohol. When the solvent is methanol or a mixture containing methanol, reduction of double bonds may take place in the absence of elemental hydrogen, the alcohol serving as the source of hydrogen. When higher alcohols are used as solvents, ester interchange is extensive.

There are differences in the effectiveness of the catalysts in each series. Addition of tin(II) chloride enhances the reactivity of dichlorobis(triphenylphosphine)platinum(II) or the analogous palladium complex[10] but does not change that of the nickel complex.[10] Mixtures of tin(II) chloride with dichlorobis(triphenylarsine)platinum(II) or potassium tetrachloroplatinate(II) are effective catalysts, but mixtures of tin(II) chloride with dichlorobis(triphenylarsine)palladium(II) or potassium tetrachloropalladate(II) are not. On the other hand, both dicyanobis(triphenylphosphine)palladium(II) and dicyanobis(triphenylarsine)palladium(II) alone are effective catalysts, but the dicyanoplatinum analogs are not.



Figures 1–6. Infrared spectra of hydrogenated methyl linoleate in CS_2 (left-hand curves) and gas chromatograms of hydrogenated methyl linoleate on 20% diethylene glycol succinate at 206° (right-hand curves): top, expt 57; center, expt 15; bottom, expt 54.

Most of the studies which we have made have been designed to test the generality of the catalytic effects, and, thus far, relatively little attention has been paid to bonding, kinetics, the isolation of intermediates and derivatives, and other mechanistic features. These aspects of the work are now being studied, both in our laboratory and at the Northern Utilization Research Laboratory of the U. S. Department of Agriculture. Some of the results will be reported from the two laboratories separately, and some jointly.

Experimental Section

Materials and Analyses. The chemicals used were of chemical grades. Methyl oleate and methyl linoleate were obtained from the Hormel Institute, University of Minnesota.

The infrared absorption of the esters containing isolated double bonds was measured by the standard method on a Beckman IR 5A spectrophotometer. The amount of isolated *trans* double bond was evaluated by using methyl elaidate as a standard.[14] Typical examples are shown in Figures 1 and 5. However, the evaluation of the reaction products containing conjugated dienes seems to involve some error caused by overlap of the peaks of conjugated dienes as shown in Figure 3.

Gas chromatographic analyses of the reaction products were carried out on a 10 ft × $^1/_8$ in. copper column packed with 20% diethylene glycol succinate on Chromosorb W (60–80 mesh). A Wilkins Aerograph Hi-Fy flame ionization detector was employed. Analyses were carried out at *ca.* 206° using nitrogen gas (flow rate 30 ml/min).

Typical examples are shown in Figures 2, 4, and 6.

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(9) H. Itatani and J. C. Bailar, Jr., to be published.

(10) Part V of this series; see ref 1a.

(11) H. Itatani and H. Tayim, unpublished observations.

(12) Unpublished observations; methyl *cis,cis*-9,15-octadecadienoate and ethyl arachidonate both give monoenates.

(13) E. N. Frankel, E. A. Emken, H. Itatani, and J. C. Bailar, Jr., *J. Org. Chem.*, in press.

(14) Official and Tentative Methods of American Oil Chemists' Society, 2nd ed, Chicago, Ill., cd-14-61.

Table I. Analytical Data of New Platinum Complexes[a]

Compound	Formula	Mp, °C	Str frequencies,[c] cm^{-1} Pt-H	Str frequencies,[c] cm^{-1} Others	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found	Cl, % Calcd	Cl, % Found	Br, % Calcd	Br, % Found	Solubility[e]
$PtHCN((C_6H_5)_3P)_2$	$C_{37}H_{31}NP_2Pt$	>185[b]	2075	CN, 2160	59.50	59.72	4.18	4.17	1.87	1.93					Sol in B-Me, insol in acetone, CCl_4
$PtHSnCl_3((C_6H_5)_3P)^d$	$C_{36}H_{31}Cl_3SnPt$	154-156	2080 s 2120 w		45.61	45.98	3.30	3.51			11.24	10.70			Sol in B-Me, CH_2Cl_2, CH_3NO_2, acetone
$PtHNO_2((C_6H_5)_3P)_2$	$C_{36}H_{31}NO_2P_2Pt$	163-165	2180	NO_2, 1360	56.37	56.74	4.07	4.19	1.82	1.61					Sol in B, insol in acetone, CCl_4
$PtHCl((C_6H_5)_3P)_2^d$	$C_{36}H_{31}P_2ClPt$	215-220	2220		57.17	56.92	4.13	4.14			4.68	4.68			Sol in B, insol CCl_4, acetone
$PtHBr((C_6H_5)_3P)_2$	$C_{36}H_{31}P_2BrPt$	191-193	2280		54.00	54.37	3.91	4.03					9.97	9.79	Sol in B, CCl_4
$PtHSCN((C_6H_5)_3P)_2$	$C_{37}H_{31}NSP_2Pt$	203-204	2250	CN, 2080	57.05	57.19	4.02	4.04	1.66	1.67					Sol in B, insol in CCl_4
$PtHOCN((C_6H_5)_3P)_2$	$C_{37}H_{31}NOP_2Pt$	188-190	2260	CN, 2225	58.26	59.16	4.09	4.05	1.83	1.75					Sol in B, acetone
$PtBr_2((C_6H_5)_3P)_2$	$C_{36}H_{30}P_2Br_2Pt$	302-305			49.15	48.31	3.34	3.45					18.18	17.72	Insol in CCl_4
$PtCl_2((C_6H_5O)_3P)_2^d$	$C_{36}H_{30}O_6P_2Cl_2Pt$	192-194			48.76	48.99	3.41	3.39			7.99	7.83			Sol in B, insol in CCl_4
$Pt(CN)_2((C_6H_5)_3P)_2$	$C_{38}H_{30}N_2P_2Pt$	>325[b]		CN, 2130	59.14	59.27	3.92	3.88	3.63	3.51					Sol in B-Me
$Pt(CN)_2((C_6H_5)_3As)_2$	$C_{38}H_{30}N_2As_2Pt$	293-294		CN, 2130	53.09	53.04	3.52	3.60	3.26	3.03					Sol in B-Me
$PtHCl((C_6H_5)_3As)_2$	$C_{36}H_{31}ClAs_2Pt$	187-190	2170		51.22	51.97	3.70	3.85			4.20	4.47			Sol in B, insol in CCl_4

[a] These materials were dried over P_2O_5 at 100° *in vacuo*. [b] Decomposes. [c] Infrared spectra were measured in hexachlorobutadiene mull. [d] These compounds have been reported previously. [e] These compounds are soluble in $CHCl_3$ but insoluble in water, diethyl ether, and *n*-heptane; B = benzene, Me = methanol, B-Me = the mixture of benzene and methanol.

Preparation of Platinum Complexes. Dichlorobis(triphenylphosphine)platinum(II),[15,16] hydridochlorobis(triphenylphosphine)platinum(II),[15] dichlorobis(triphenylarsine)platinum(II),[16,17] dichlorobis(triphenylstibine)platinum(II),[16,18] dichlorobis(tributylphosphine)platinum(II),[16] dichloroethylenediamineplatinum(II),[19] tetrakis(triphenylphosphine)platinum(0),[17] and tetrakis(triphenylarsine)platinum(0)[17] were prepared by methods described in the literature. Data on the other compounds are given in Table I.

Dicyanobis(triphenylphosphine)platinum(II), $Pt(CN)_2((C_6H_5)_3P)_2$. Dichlorobis(triphenylphosphine)platinum(II) (3.0 g, 3.8 mmoles) was added to a solution of potassium cyanide (0.618 g, 9.5 mmoles) in methanol (100 ml). The powder did not dissolve but was kept in suspension at 50° with constant stirring. During the course of 5 hr, white crystals separated. These were filtered, washed with water and methanol, and dissolved in a hot solution of benzene (30 ml) and methanol (15 ml). The crystals (1.4 g) which separated on cooling were filtered and washed with diethyl ether. Analytical data are shown in Table I.

Dicyanobis(triphenylarsine)platinum(II), $Pt(CN)_2((C_6H_5)_3As)_2$. Dichlorobis(triphenylarsine)platinum(II) (2.0 g, 2.3 mmoles), was added to a solution of potassium cyanide (0.37 g, 5.7 mmoles) in benzene (20 ml) and methanol (80 ml). The suspension was kept at 50° for 5 hr with constant stirring. After addition of water (30 ml), the insoluble powder was filtered and washed with water. This powder was twice recrystallized by dissolving in benzene and methanol (4:1 v/v) and precipitating by addition of ethyl ether.

Hydridocyanobis(triphenylphosphine)platinum(II), $PtHCN((C_6H_5)_3P)_2$. To a solution of hydridochlorobis(triphenylphosphine)platinum(II) (2.0 g, 2.6 mmoles) in methanol (20 ml) and benzene (40 ml) was added a solution of potassium cyanide (0.21 g, 32 mmoles) in methanol (80 ml). After 2 hr at 50° with constant stirring, the solution was concentrated to *ca.* 20 ml whereupon crystals began to separate. To the solution was added 4:1 v/v methanol–water (50 ml). The crystals which separated on cooling were filtered and washed with water and diethyl ether. The material was purified by dissolving it (1.43 g) in 100 ml of hot benzene and adding 100 ml of *n*-heptane to the solution. On cooling, the solution deposited 0.93 g of white crystals. A second crop (0.19 g) was recovered from the mother liquor.

Hydridothiocyanatobis(triphenylphosphine)platinum(II), $PtHSCN((C_6H_5)_3P)_2$. A suspension of $PtHCl((C_6H_5)_3P)_2$ (2.0 g, 2.6 mmoles) in a solution of potassium thiocyanate (0.308 g, 3.2 mmoles) in methanol (100 ml) was stirred at 50° for 3 hr. The white crystals which formed were filtered and washed with water, methanol, and finally with ether. *n*-Heptane (100 ml) was added to a solution of this product (1.97 g) in warm benzene (80 ml). On cooling, crystals (1.77 g) separated from solution.

Hydridonitrobis(triphenylphosphine)platinum(II), $PtHNO_2((C_6H_5)_3P)_2$. A solution of potassium nitrite (0.092 g, 1.3 mmoles) in methanol (40 ml) was added to a solution of $PtHCl((C_6H_5)_3P)_2$ (1.0 g, 1.1 mmoles) in benzene (20 ml). The mixture was stirred at 50° for 2 hr and then concentrated to about 30 ml, whereupon crystals started to form. A mixture of methanol (20 ml) and water (20 ml) was added and the solution was allowed to cool. The white crystals which were deposited were filtered, washed with water and ether, and recrystallized from a mixture of benzene (15 ml) and ether (100 ml) giving 0.59 g of pure substance.

Hydridocyanatobis(triphenylphosphine)platinum(II), $PtHOCN((C_6H_5)_3P)_2$. A suspension of $PtHCl((C_6H_5)_3P)_2$ (0.5 g, 0.66 mmole) and potassium cyanate (0.064 g, 0.79 mmole) in methanol (25 ml) was stirred at 50° for 3 hr. After cooling in ice, the crystals were filtered and washed with water, giving a product (0.45 g), which was recrystallized from benzene (10 ml) and *n*-heptane (14 ml). The yield was 0.37 g.

Hydridotrichlorostannatobis(triphenylphosphine)platinum(II), $PtHSnCl_3((C_6H_5)_3P)_2$. It has been found that the method described earlier[15] gives better yields if the solution of $PtHCl((C_6H_5)_3P)_2$ and tin(II) chloride is refluxed for 5 min. Another method of preparation is as follows. The solutions of $PtHCl((C_6H_5)_3P)_2$ (1.0 g, 1.3 mmoles) and tin(II) chloride dihydrate (1.0 g, 4.4 mmoles) in acetone (15 ml) are mixed and heated gently on a steam bath for 5 min. After filtration, a powder is precipitated by the addition of diethyl ether (50 ml). This (0.9 g) is filtered, washed

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(15) Part I of this series; see ref 1a.

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Table II. Hydrogenation of Methyl Linoleate (1.0 g, 3.4 mmoles) Using Platinum Complexes (0.34 mmole) in Benzene (30 ml) and Methanol (20 ml)[a]

Expt	Catalyst	Infrared analysis, % *trans*[b]	Glpc analysis,[c] % S	M	D	c–t	t–t	Ppt[d]
1	$PtCl_2((C_6H_5)_3P)_2$	10.3		4.1	95.9			–
2	$PtCl_2((C_6H_5)_3As)_2$	43.6		47.5	48.0	4.5		+
3	$PtCl_2((C_6H_5)_3Sb)_2$	2.8			100			+
4	$PtCl_2((C_6H_5O)_3P)_2$	. . .[e]		24.1	56.4	19.5		+
5	$PtHCN((C_6H_5)_3P)_2$	2.6			100			–
6	$PtHSnCl_3((C_6H_5)_3P)_2$	33.3		3.5	65.8	27.2	3.5	–
7	$PtHNO_2((C_6H_5)_3P)_2$	3.9			100			–
8	$PtHCl((C_6H_5)_3P)_2$	5.8		3.8	96.2			–
9	$PtHSCN((C_6H_5)_3P)_2$	3.4		0.7	99.3			–
10	$PtHOCN((C_6H_5)_3P)_2$	5.0			100			–
11	$Pt(CN)_2((C_6H_5)_3P)_2$	1.4			100			–
12	$Pt(CN)_2((C_6H_5)_3As)_2$	6.8			100			–
13	$Pt((C_6H_5)_3P)_4$	5.7			100			–
14	$Pt((C_6H_5)_3As)_4$	6.3		4.2	95.8			+

[a] At 90° for 5 hr, 39.1 atm of hydrogen. [b] *trans* isomer, per cent calculated as elaidate. [c] Abbreviations: S, stearate; M, monoenate including oleate; D, dienoate including linoleate; c–t, *cis–trans* conjugated dienoate; t–t, *trans–trans* conjugated dienoate. [d] + means that a precipitate was observed after hydrogenation due to the decomposition of catalyst; – means that the solution was homogeneous after hydrogenation. [e] It was difficult to determine *trans* per cent.

with ether, and purified by dissolving it in nitromethane (15 ml) and precipitating by the addition of *n*-heptane (50 ml) and ether (50 ml); yield, 0.6 g.

Dichlorobis(triphenyl phosphito)platinum(II), $PtCl_2((C_6H_5O)_3P)_2$. The preparation of this compound from platinum(II) chloride has been reported, and the melting point has been given as 155°[20] and as 190–191°.[21] We find a melting point of 192–194°. We have improved the method as follows. A vigorously stirred mixture of triphenyl phosphite (2.0 g, 6.4 mmoles) and potassium tetrachloroplatinate(II) (1.0 g, 2.4 mmoles) was kept at 210–220° for several minutes, during which time the red mixture became white. After cooling to room temperature, warm benzene (10 ml) was added to dissolve the unchanged triphenyl phosphite. The insoluble residue (1.4 g) and a little (0.2 g) material which precipitated from the filtrate were combined, and, after washing with water and methanol, the material was recrystallized twice from benzene (40 ml); yield, 1.0 g.

Dibromobis(triphenylphosphine)platinum(II), $PtBr_2((C_6H_5)_3P)_2$. Potassium dioxalatoplatinate(II) (2.85, g, 6.3 mmoles), obtained from potassium hexachloroplatinate(IV),[22] was dissolved in 40 ml of 10% aqueous hydrobromic acid, and the solution was evaporated to 10 ml. The oxalic acid crystals which formed on cooling were filtered off. The filtrate was evaporated to dryness and the residue was dissolved in 10 ml of water. This solution was added dropwise to warm (*ca.* 60°) ethanol (70 ml) containing triphenylphosphine (3.3 g, 12.6 mmoles) with constant stirring. Yellow crystals (2.8 g) melting at 302–305° precipitated immediately. These were washed successively with water, ethanol, and ether; 1 g of the material was recrystallized from chloroform (100 ml) and diethyl ether (50 ml); yield, 0.66 g.

Hydridobromobis(triphenylphosphine)platinum(II), $PtHBr((C_6H_6)_3P)_2$. A mixture of hydrazine hydrate (0.42 g) and dibromobis(triphenylphosphine)platinum(II) was dissolved in 25 ml of boiling ethanol. Upon neutralization with concentrated aqueous hydrobromic acid and addition of water (10 ml), 0.3 g of crystals separated. These were recrystallized from benzene (3 ml) and ethanol (10 ml) (yield of pure product, 0.23 g).

Hydridochlorobis(triphenylarsine)platinum(II), $PtHCl((C_6H_5)_3As)_2$. A mixture of tetrakis(triphenylarsine)platinum(0) (1.0 g)[17] in benzene (5 ml) and anhydrous methanolic hydrochloric acid (1.8 *N* 4 ml) was heated on a steam bath for several minutes, and 25 ml of ethanol was added. The white needles which separated on cooling (0.25 g) were washed with ethanol and ether.

Formation of the Hydridoplatinum Complex by Reactions under Hydrogen Pressure. A mixture of $PtCl_6((C_6H_5)_3P)_2$ (1.0 g, 1.3 mmoles) and $SnCl_2{\cdot}2H_2O$ (1.0 g, 4.4 mmoles) in methanol (50 ml) was heated at 90° in a rocking autoclave under 39.1 atm of hydrogen for 3 hr. The reaction vessel was left overnight to cool to room temperature. The crystals which had formed were filtered and washed with ether, giving crude *trans*-hydridochlorobis(triphenylphosphine)platinum(II) (0.7 g),[11] which was recrystallized from benzene and methanol.

A mixture of $PtCl_2((C_6H_5)_3P)_2$ (0.5 g) and $SnCl_2{\cdot}2H_2O$ (1.0 g) was treated under the same conditions. A maize-colored powder and a black powder were found in the reaction mixture. The maize-colored material was dissolved in acetone and precipitated by adding a 1:1 mixture of ether and *n*-heptane. This material is shown by its infrared spectrum and its melting point to be identical with $PtH(SnCl_3)((C_6H_5)_3P)_2$.

In expt 1, the reduced solution was evaporated to dryness. The residue was washed with ether and recrystallized from a mixture of benzene and ethanol. It was shown to be identical with known samples of hydridochlorobis(triphenylphosphine)platinum(II).[15]

Hydrogenation of Methyl Linoleate under Various Conditions. Methyl linoleate (1.0 g, 3.4 mmoles) was hydrogenated in toluene (30 ml) and 1-butanol (20 ml) under 39.1 atm of hydrogen at 90° for 12 hr, using mixtures of tin(II) chloride dihydrate and platinum complexes as catalysts. Ester exchange reactions of methyl linoleate and the butanol were observed, as shown in expt 54 and 55 in Table VII.

Methyl linoleate (2.0 g, 6.8 mmoles) in benzene (30 ml) and methanol (20 ml) was hydrogenated with a mixture of tin(II) chloride dihydrate (1.0 g, 4.4 mmoles) and $PtCl_2((C_6H_5)_3P)_2$ (1.0 g, 1.26 mmoles) (expt 49). The resulting solution was evaporated on a steam bath, and the organic materials were extracted with diethyl ether. The reddish oily residue was dissolved in benzene (30 ml) and methanol (20 ml) containing methyl linoleate (2.0 g), and the mixture was hydrogenated again under the same conditions (expt 50). The recovered catalyst is an effective catalyst, but not as effective as the original material, probably owing to the loss of some tin chloride during the recovery of the catalyst. Repetition of the experiment, with care to avoid this difficulty, gave a catalyst which was the same as the original (expt 51–53). This indicates that the catalytic platinum complex was in solution and that it was not decomposed during the hydrogenation or the subsequent treatment.

Reactions of Methyl Oleate and Methyl Linoleate. The reactions of methyl oleate (1.0 g, 3.4 mmoles) and methyl linoleate (1.0 g, 3.4 mmoles) in mixtures of benzene (30 ml) and methanol (20 ml) were carried out in a rocking autoclave as already described.[6] Mixtures of the platinum complex (0.34 mmole) and group IVa halides (1.7 mmoles) such as tin(II) dichloride dihydrate were used as catalysts. In some cases, reactions were run under nitrogen pressure in place of hydrogen pressure. After hydrogenation, the reaction mixture was heated on a steam bath to remove the solvent. The residue was extracted twice with diethyl ether (total 100 ml), and the ethereal solution was washed with aqueous hydrochloric acid (5%, 15 ml), water, aqueous sodium bicarbonate (5%, 15 ml), and again with water (30 ml). This solution was dried over anhydrous sodium sulfate and purified by passing through a column (diameter 0.55 mm) packed with acid-washed alumina

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Table III. Enhancement of Catalysis by Adding Halides of Group IV Elements[a,b]

Expt	Catalysts	Infrared, analysis, % *trans*	Glpc analysis, %[c] U	S	M	D	c–t	t–t	Ppt
15	$PtCl_2((C_6H_5)_3P)_2 + SnCl_2 \cdot 2H_2O$	64.6			14.4	42.2	20.4	22.8	–
16	$PtCl_2((C_6H_5)_3P)_2 + SnCl_4$[e]	91.0	0.6		29.3	50.3	7.3	12.6	–
17	$PtCl_2((C_6H_5)_3P)_2 + GeCl_2 + HCl$[d]	24.4	5.8		13.4	78.4	1.0	0.7	–
18	$PtCl_2((C_6H_5)_3P)_2 + GeCl_4$	17.6	3.3		12.6	81.8	2.3		+
19	$PtCl_2((C_6H_5)_3P)_2 + PbCl_2 + HCl$[d]	13.2	8.0		8.4	83.6			–
20	$PtCl_2((C_6H_5)_3P)_2 + SiCl_4$	11.6	6.0		10.7	83.3			–
21	$PtCl_2((C_6H_5)_3P)_2 + SiHCl_3$	6.3			10.0	90.0			–

[a] Conditions: methyl linoleate (3.4 mmoles), platinum complexes (0.34 mmole), group IV halide (1.7 mmoles), at 90° for 5 hr, 39.1 atm of hydrogen in benzene (30 ml) and methanol (20 ml). [b] Notations in this table are the same as those in Table II. [c] U = unknown components. [d] Anhydrous hydrogen chloride (3.5 mmoles). [e] In this case, reaction time is 3 hr.

Table IV. Effect of Varying the Ligands of Platinum Complexes Containing Tin(II) Halides[a,b]

Expt	*Catalysts*	Infrared analysis, % *trans*	Glpc analysis, % *U*	*S*	*M*	*D*	c–t	t–t	*Ppt*
15	$PtCl_2((C_6H_5)_3P)_2 + SnCl_2 \cdot 2H_2O$	64.6		1	14.4	42.2	20.4	22.8	–
22	$PtHCl((C_6H_5)_3P)_2 + SnCl_2 \cdot 2H_2O$	60.6			13.8	40.3	21.6	21.2	–
23	$PtCl_2((C_6H_5)_3As)_2 + SnCl_2 \cdot 2H_2O$	74.5			66.5	19.6	6.6	7.3	+
24	Ppt from expt 23[c]	33.9			3.2	96.8			
25	$PtCl_2((C_6H_5O)_3P)_2 + SnCl_2 \cdot 2H_2O$	81.8		6.2	87.9	5.9			–
26	$PtCl_2((C_6H_5)_3Sb)_2 + SnCl_2 \cdot 2H_2O$	77.2	1.4		14.5	74.6	6.8	1.8	+
27	$PtCl_2(Bu_3P)_2 + SnCl_2 \cdot 2H_2O$	39.2			2.4	78.4	11.2	8.0	–
28	$PtCl_2en + SnCl_2 \cdot 2H_2O$	5.1	2.3			97.7			+
29	$K_2PtCl_4 + SnCl_2 \cdot 2H_2O$	81.2		1.2	43.2	35.2	13.3	7.1	+
30	$PtBr_2((C_6H_5)_3P)_2 + SnBr_2$	74.6			24.6	50.0	10.0	15.3	+

[a] Conditions: methyl linoleate (3.4 mmoles), platinum complexes (0.34 mmole), tin(II) halides (1.7 mmoles) in benzene (30 ml) and methanol (20 ml) at 90° for 5 hr at 39.1 atm of hydrogen. [b] Notations in this table are the same as those in Tables II and III. [c] A black precipitate obtained from expt 23 was separated from solution by decantation, washed with methanol, and used again.

Table V. Isomerization of Methyl Oleate (3.4 mmoles) Using Platinum Complexes (0.34 mmole) with Tin(II) Halide (1.7 mmoles) in Benzene (30 ml) and Methanol (20 ml)[a,b]

Expt	Catalysts	*trans* %	S, %	M, %	Ppt
31	$PtCl_2((C_6H_5)_3P)_2 + SnCl_2 \cdot 2H_2O$	80.2		100	–
32	$PtHCl((C_6H_5)_3P)_2 + SnCl_2 \cdot 2H_2O$	78.6		100	–
33	$PtCl_2((C_6H_5)_3As)_2 + SnCl_2 \cdot 2H_2O$	70.0	2.5	97.5	+
34	$PtCl_2((C_6H_5O)_3P)_2 + SnCl_2 \cdot 2H_2O$	76.5	6.4	93.6	+
35	$PtCl_2((C_6H_5)_3Sb)_2 + SnCl_2 \cdot 2H_2O$	52.0		100	+
36	$PtBr_2((C_6H_5)_3P)_2 + SnBr_2$	72.3		100	+
37	$K_2PtCl_4 + SnCl_2 \cdot 2H_2O$	65.0		100	+

[a] At 90° for 5 hr at 39.1 atm of hydrogen. [b] Notations in this table are the same as those in Table II.

Table VI. Reactions in an Inert Atmosphere (Nitrogen Pressure, 23.8 Atm)[a]

Expt	Substrate	Catalysts	*trans* %	Glc analysis, % S	M	D	t–t	c–t	Ppt
38	Linoleate	$PtCl_2((C_6H_5)_3P)_2 + SnCl_2 \cdot 2H_2O$	61.2		4.9	48.3	21.0	25.8	–
39		$PtHCl((C_6H_5)_3P)_2 + SnCl_2 \cdot 2H_2O$	35.4			59.3	25.0	15.7	–
40		$PtCl_2((C_6H_5)_3As)_2 + SnCl_2 \cdot 2H_2O$	61.6		51.6	24.8	9.7	13.9	+
41		$K_2PtCl_4 + SnCl_2 \cdot 2H_2O$	12.4			100			+
42	Oleate	$PtCl_2((C_5H_5)_3P)_2 + SnCl_2 \cdot 2H_2O$	79.3		100				–
43		$PtHCl((C_6H_5)_3P)_2 + SnCl_2 \cdot 2H_2O$	79.0		100				–
44		$PtCl_2((C_6H_5)_3As)_2 + SnCl_2 \cdot 2H_2O$	73.0		100				–
45		$K_2PtCl_4 + SnCl_2 \cdot 2H_2O$	2.7		100				+

[a] Conditions: methyl linoleate or methyl oleate (3.4 mmoles), platinum complexes (0.34 mmole), tin(II) halides (1.7 mmoles) in benzene (30 ml) and methanol (20 ml) at 90° for 5 hr.

(30 ml). After treatment with charcoal to remove the colored material, if necessary, the solution was evaporated to dryness *in vacuo*, giving 70–90% yields of oil. The results are shown in Tables II–VI.

Results and Discussion

The results of experiments with methyl oleate and methyl linoleate using $PtCl_2L_2$ and $PtHClL_2$ (L = organophosphine, -arsine, or -stibine) are shown in Tables II–VII.

Enhancement of Catalysis by Adding Halides of Group IV Elements. In order to investigate the effect of varying the ligands bonded to the platinum atom as well as the effect of adding group IVa halides to the platinum complexes, hydrogenation of methyl linoleate was carried out under conditions that give partially hydrogenated esters. The results are shown in Tables II and III. Hydrogenation of methyl linoleate with $PtCl_2((C_6H_5)_3P)_2$ (complex *I*) gave only 4.1% monoenate (expt 1), but addition of tin(II) chloride increased the yield of monoenate to 14.4% and conjugated dienes

Table VII. Reactions of Methyl Linoleate under Various Conditions at 90° under 39.1 Atm of Hydrogen[a]

Expt	Lino-leate, mmoles	Catalysts (mmoles)	Solvent (ml)	Reaction time, hr	*trans* %	Glpc analysis, %					Ppt
						S	M	D	c–t	t–t	
46	3.4	$PtCl_2((C_6H_5)_3P)_2$ (0.34) + $SnCl_2 \cdot 2H_2O$ (1.7)	C_6H_6 (30), MeOH (20)	11	73.5		36.8	31.2	10.8	21.2	–
47	3.4	As above	C_6H_6 (15), MeOH (10)	5	89.5		65.4	23.7		10.9	–
48	3.4	$PtCl_2((C_6H_5)_3P)_2$ (0.63) + $SnCl_2 \cdot 2H_2O$ (4.4)	C_6H_6 (30), MeOH (20)	10	87.8	0.5	91.1	8.4			–
49	6.8	$PtCl_2((C_6H_5)_3P)_2$ (1.26) + $SnCl_2 \cdot 2H_2O$ (4.4)	As above	3	80.9		73.5	20.8	2.2	3.5	–
50	6.8	Recovered catalyst from expt 49	As above	3	66.6		28.9	24.6	15.2	31.7	–
51	6.8	$PtCl_2((C_6H_5)_3P)_2$ (1.26) + $SnCl_2 \cdot 2H_2O$ (4.4)	As above	3	75.3		38.6	25.4	12.7	23.3	
52	6.8	Recovered from expt 51[d]	As above	3	72.2		38.1	24.2	10.9	26.8	
53	6.8	Recovered from expt 51[e]	As above	3	66.5		36.2	25.6	12.8	25.4	
54	3.4	$PtCl_2((C_6H_5)_3P)_2$ (0.63) + $SnCl_2 \cdot 2H_2O$ (4.4)	Toluene (30), 1-butanol (20)	12	78.1		Me 10.8,[b] Bu 90.2				+
55	3.4	$PtCl_2((C_6H_5)_3As)_2$ (0.68) + $SnCl_2 \cdot 2H_2O$ (4.4)	As above	12	43.5	Bu 18.7	Me 2.1, Bu 79.2				+
56	3.4	$PtCl_2((C_6H_5)_3P)_2$ (0.34) + $SnCl_2 \cdot 2H_2O$ (1.7) + urea[c]	C_6H_6 (30), MeOH (20)	5	81.3		35.9	40.7	9.5	13.9	–
57	3.4	$PtCl_2((C_6H_5)_3As)_2$ (0.68) + $SnCl_2 \cdot 2H_2O$ (4.4)	As above	11	59.7	2.9	92.2	4.9			+

[a] Notations in this table are the same as those in Table II. [b] Me = methyl ester, Bu = butyl ester. [c] Urea, 2.0 mmoles. [d] The solution from expt 51 was evaporated at a pressure of 0.02 mm. The ester was extracted from the remaining material with 50 ml of petroleum ether. The residue from the extraction was used as the catalyst in expt 52. [e] A repetition of expt 52, but the residue, after treatment with petroleum ether, was dissolved in 50 ml of CH_2Cl_2. After filtration, the solvent was evaporated, 4.4 ml of $SnCl_2 \cdot 2H_2O$ was added, and the material was used as the catalyst.

to 43.2% (sum of c–t and t–t, in Table III, expt 15). It has been reported earlier[6] that tin(II) chloride alone is not effective in either the hydrogenation or isomerization of soybean oil methyl ester and related compounds. Addition of halides of group IV elements to complex I results in the conversion of methyl linoleate in the following amounts (difference between D and 100% in Table III): $SnCl_2 \cdot 2H_2O$ (57.8%), $SnCl_4$ (49.7%), $GeCl_2 + HCl$ (21.6%), $GeCl_4$ (18.2%), $PbCl_2 + HCl$ (16.4%), $SiCl_4$ (16.7%), $SiHCl_3$ (10.0%). The Sn(II), Ge(II), and Pb(II) atoms seem to be combined directly to the platinum atom and cause the polarization of the platinum. In fact, the $SnCl_3$ group has been shown to behave as a strong π acceptor.[23] It has been reported that the addition of trichlorosilane to olefin is catalyzed by addition of chloroplatinic acid.[24] This was explained by assuming that the catalyst involves a low oxidation state of platinum made by reduction of chloroplatinic acid by the silicon hydride.

$$-Pt- + R_3SiH \rightleftarrows R_3Si-Pt-H$$

Effect of Varying the Ligands. The catalysis is strongly dependent upon the nature of the uncharged ligands on the platinum atom. In some cases, hydrogenation was accompanied by the formation of a black precipitate, which seems to be the group VIII metal. The black precipitate obtained from the reaction of $PtCl_2((C_6H_5)_3As)_2$ and tin(II) chloride was reused as a catalyst for hydrogenation of methyl linoleate. It gave only 3.2% methyl monoenate under the same conditions that had been employed with the original catalyst (expt 24). Also, the hydrogenation of methyl oleate using $PtCl_2((C_6H_5)_3As)_2$ and $SnCl_2 \cdot 2H_2O$ gave 2.5% of saturated compound. This may be the result of catalysis by the precipitate (expt 33). These observations indicate that heterogeneous hydrogenation caused by the black precipitate is not related to homogeneous hydrogenation catalyzed by the platinum complexes. We feel, therefore, that it is safe to assume that we are dealing here with a truly homogeneous reaction and that analogous complexes containing different ligands may be compared, even though some of them decompose during hydrogenation.

In the reaction catalyzed by tin(II) chloride and complexes of the type $PtCl_2L_2$, extents of conversion of methyl linoleate decrease in the following order: $(C_6H_5O)_3P$ (94.1%), $(C_6H_5)_3As$ (80.4%), $(C_6H_5)_3P$ (57.6%), $(C_6H_5)_3Sb$ (24.5%), Bu_3P (21.6%), en/2 (2.3%), as shown in Table IV (difference between per cent diene and 100%).

This series parallels the order of the nmr chemical shifts of nickel–phosphine complexes,[25] decreasing carbonyl stretching frequencies of nickel complexes,[26] and decreasing nitrosyl stretching frequencies of the ferrous complexes.[27] In addition, the Pt–H frequency in $PtHCl((C_6H_5)_3P)_2$ is less than that in $PtHCl((C_6H_5)_3As)_2$, in agreement with the belief that the catalyst with the weaker Pt–H bond is more effective for hydrogenation.[28]

Effect of the Halide Ion Bonded to the Platinum Atom. Hydrogenation with a mixture of dibromobis(triphenylphosphine)platinum(II) and tin(II) bromide as a catalyst is more effective than with a mixture of the complex chloride and tin(II) chloride dihydrate (expt 30 and 15). This result is not in line with the fact that the Pt–H stretching frequency of the hydridobromo complex is much higher than that of hydridochloro analog as shown in Table I. However, it is understandable if

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we assume that the Pt–H bond in the Pt–$SnBr_3$ complex is similar to that in the Pt–$SnCl_3$ complex.

Hydrogenation with Hydridoplatinum Complexes. In the course of the hydrogenation, hydride complexes seem to be formed as indicated by the fact that complex I is converted to the hydride complex either in the presence or absence of tin(II) chloride. It is also evident that catalysis by $PtHCl((C_6H_5)_3P)_2$ and tin(II) chloride is similar to that exerted by the dichloroplatinum analog and tin(II) chloride (expt 15 and 22). Complexes of the type $PtHX((C_6H_5)_3P)_2$ (where X is CN, $SnCl_3$, NO_2, Cl, SCN, and OCN) are not effective for hydrogenation as shown in Table II. The results of expt 6 again indicate the existence of the equilibrium shown by the equation

$$PtH(SnCl_3)((C_6H_5)_3P)_2 \rightleftharpoons PtHCl((C_6H_5)_3P)_2 + SnCl_2$$

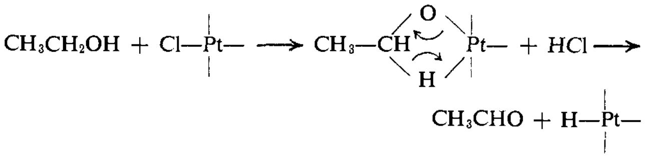
Hydrogenation becomes a major reaction only in the presence of excess tin(II) chloride. Strikingly, it has been noticed that the Pt–H bonds are remarkably sensitive to the nature of the ligands bonded to the platinum atom, and the order of decreasing Pt–H frequencies is related to decreasing Pt–H bond strength.[28] As the ligand (L) is changed, the Pt–H stretching frequencies (cm^{-1}) in $PtHX((C_6H_5)_3P)_2$ increase in the following order: X = CN (2075), $SnCl_3$ (2080 s, 2120 w), NO_2 (2180), Cl (2220), SCN (2250), OCN (2260), Br (2280). These complexes seem to be of the *trans* configuration, and this order is in good agreement with that reported in the literature,[28–30] except in the case of the hydridobromo complex. The Pt–H stretching frequency of hydridothiocyanatobis(triethylphosphine)platinum(II) was reported to shift from 2195 (Nujol mull) to 2112 cm^{-1} (benzene solution).[29] Although CN^- is also a powerful π acceptor,[23] the hydridocyanoplatinum complex is not effective for hydrogenation.

Neither dicyano complexes such as $Pt(CN)_2((C_6H_5)_3As)_2$ and $Pt(CN)_2((C_6H_5)_3P)_2$ nor zerovalent complexes such as $((C_6H_5)_3As)_4Pt$ and $((C_6H_5)_3P)_4Pt$ are effective for hydrogenation. However, the dicyanopalladium analogs are effective.[10] The differences in catalysis between Pt and Pd complexes are due to the easier expansion of the coordination sphere of the Pd ion as compared with that of the Pt ion.[31]

Isomerization of Methyl Oleate. Using a variety of platinum complexes, methyl oleate, which has the *cis* configuration, was converted to the *trans* isomer but not to the saturated compound, stearate (Table V).

The formation of small amounts of stearate in expt 33 and 34 probably is due to the catalytic action of the platinum black formed during the hydrogenation. It can be seen from the results of expt 15 that isomerization to the *trans* form proceeds much more rapidly than the hydrogenation. Somewhat different contents of *trans* isomers were obtained by the action of catalysts containing a variety of complexing agents (expt 31 to 35).

Reactions under Nitrogen Pressure. In an inert atmosphere (nitrogen pressure), a mixture of tin chloride with either complex I or $PtCl_2((C_6H_5)_3As)_2$ is effective for both hydrogenation of linoleate and isomerization of oleate as shown in Table VI. The activated hydrogen is supplied by the solvent, methanol. Hydride ion transfer from alcohol to metal ion has been observed in platinum[29] and palladium complexes[10] as described by the equation



$$CH_3CH_2OH + Cl{-}\overset{|}{\underset{|}{Pt}}{-} \longrightarrow CH_3{-}CH\overset{O}{\underset{H}{\rightleftharpoons}}\overset{|}{\underset{|}{Pt}}{-} + HCl \longrightarrow CH_3CHO + H{-}\overset{|}{\underset{|}{Pt}}{-}$$

Reaction with a Mixture of Potassium Tetrachloroplatinate(II) and Tin(II) Chloride Dihydrate as the Catalyst. Mixtures of chloroplatinic acid and tin(II) chloride are reported to be effective catalysts for the hydrogenation of ethylene.[6,8] The five-coordinated complex $[Pt(SnCl_3)_5]^{3-}$ [30] and the cyclooctadiene derivative $(C_8H_{12})_3Pt_3SnCl_6$[32] have been isolated. We have found that under certain conditions, a mixture of K_2PtCl_4 and $SnCl_2 \cdot 2H_2O$ is also effective for hydrogenation of linoleate and isomerization of oleate (expt 29 and 37). However, this mixture differs from the other platinum catalysts in that it is not effective in the absence of elemental hydrogen (expt 41 and 45).

Catalysis under Various Conditions. Selective hydrogenation depends to a considerable extent upon the temperature.[6] In addition, the concentration of the catalyst is important. Doubling the concentration of catalyst increases the formation of monoene from 14.6 to 65.4% (expt 15 and 47). Addition of urea to the solution did not result in any differences in hydrogenation (expt 56). In addition, the catalytic activity of these complexes is sharply dependent upon the solvent.[33]

To test the catalytic stability of the mixture of tin chloride and complex I, a sample of it was used again for hydrogenation of methyl linoleate. After each hydrogenation, the catalyst was separated from organic materials and was found to be still effective for hydrogenation (expt 49–53). In the first experiment of this kind (expt 49 and 50), the recovered catalyst was found to be less effective than the new catalyst. This was probably due to a loss of tin chloride during the recovery process. A second run, avoiding this difficulty, showed that recovered catalyst is as effective as the new material.

Ester Exchange Reaction. Reactions of methyl linoleate with tin chloride and either complex I or $PtCl_2((C_6H_5)_3As)_2$ were accompanied by an ester exchange reaction from the methyl ester to the butyl ester during the course of hydrogenation in a mixture of 1-butanol and toluene (expt 54 and 55). This reaction was also observed in catalysis with the palladium analogs.[10] Typical catalytic reactions of complex I and $PtCl_2((C_6H_5)_3As)_2$ with tin chloride can be summarized in the following observations.

1. A single double bond such as that of oleate is not hydrogenated but is isomerized from the *cis* to the *trans* configuration.

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(33) The hydrogenation of methyl linoleate with complex I and tin(II) chloride under the conditions described in Table III gave methyl monoenate in the following order using various solvents: CH_2Cl_2 (93.2%), CH_3NO_2 (32.6%), tetrahydrofuran (14.8%), and benzene–methanol (14.4%). Methanol, which is able to coordinate to metal ions, is less favorable as a solvent than is methylene chloride, which has very weak coordinating ability. The use of methylene chloride was suggested by Dr. Hassan Tayim.

2. Migration of double bonds in methyl linoleate occurs to form conjugated dienes which are then hydrogenated selectively to the monoenes.
3. Migration of double bonds is accompanied by *cis–trans* isomerization.
4. Ester exchange reactions take place in butanol solution.
5. Active hydrogen can be supplied by hydrogen gas or by a solvent such as methanol; in that case, hydrogenation takes place under nitrogen pressure as well as under hydrogen pressure.

Possible Mechanism

Generally, catalytic reaction with the platinum complexes is enhanced by the addition of halides of group IV elements. The first step in the course of hydrogenation seems to be the formation of a hydride complex. This is suggested by the isolation of a hydride complex from the reaction with complex I under pressure. A mixture of tin chloride and complex I containing a relatively small amount of tin chloride also gave a hydridochloro complex, $PtHXL_2$, but in the presence of excess tin chloride the hydridotrichlorostannato complex, $PtHSnCl_3L_2$, was formed. This suggests the equilibrium

$$PtHCl((C_6H_5)_3P)_2 + SnCl_2 \rightleftarrows PtHSnCl_3((C_6H_5)_3P)_2$$

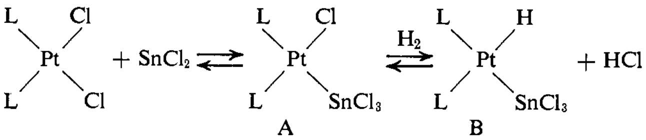
This hypothesis is confirmed by experiments in which it was shown that more concentrated solutions of the catalysts are more favorable for hydrogenation and that excess amounts of tin chloride are required for hydrogenation.

The driving force of the catalysis seems to be the formation of a hydridoplatinum complex which has a labile Pt–H bond. The lability of this bond is effected by σ bonding from the phosphine or arsine to the platinum with some contribution of strong π bonding. The more labile the Pt–H bond, the more effective is the hydrogenation of linoleate. In addition, the reactivity of the hydrido complex is enhanced by π-acceptor ligands such as $SnCl_3$ and $SnBr_3$.

The hydrido complex allows expansion of the coordination sphere and the formation of intermediates which contain unsaturated compounds as ligands. Reasonable reaction intermediates of transition metal complexes have been suggested,[5,30] but the reactivities of those catalysts are quite different from those of the platinum catalysts reported here. However, the activation of Rh and Ir complexes is probably similar to that of our platinum complexes. A possible, but speculative, mechanism can be described as shown in Chart I.

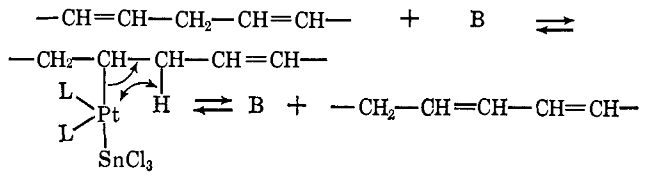
Chart I

Activation of the catalysts

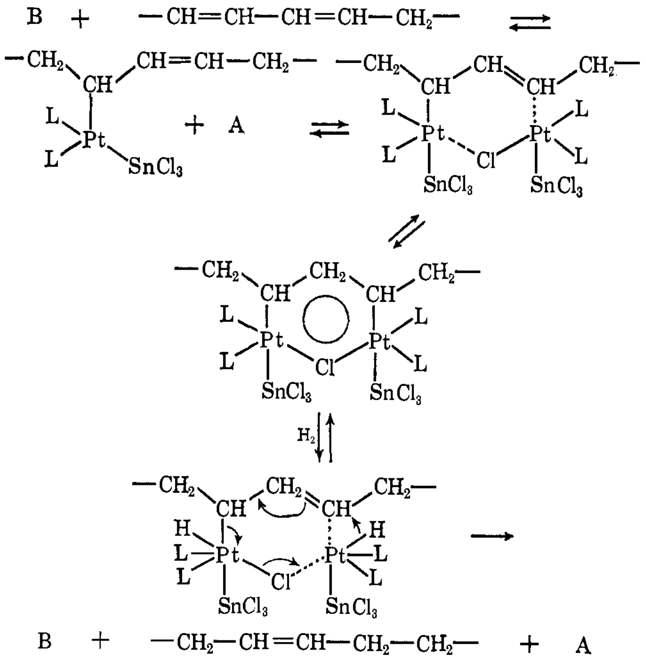


($L = (C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, $(C_6H_5O)_3P$, etc.)

Isomerization and migration of double bonds



Selective hydrogenation of conjugated dienes



The proposed allylic platinum intermediate which was isolated[34] is plausible in view of the analogous π-allylic platinum compound[35] and butadiene-bridged platinum compound[36] already reported. Chlorine-bridged complexes have been shown to be effective for isomerization reactions of olefins.[37]

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(34) Unpublished result.

(35) G. W. Parshall, *Z. Naturforsch.*, **18b**, 772 (1963).

(36) P. E. Slade, Jr., and H. B. Jonassen, *J. Am. Chem. Soc.*, **79**, 1277 (1957).

(37) N. R. Davies, *Nature*, **201**, 490 (1964); R. Cramer, *ibid.*, **87**, 4717 (1965).