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Platinum Chloride–Diphosphine–Tin(II) Halide Systems as Active and Selective Hydroformylation Catalysts

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The hydroformylation of 1-alkenes was efficiently catalyzed by $PtCl_2$–diphosphine–SnX_2 systems whose diphosphines were 1,4-bis(diphenylphosphino)butane derivatives with rigid ring skeletons. The effects of the structure of diphosphines, the P/Pt atomic ratio, the sort of tin(II) halide or solvent, the reaction variables, and the structure of olefins on the relative rate and the product distribution were investigated. A higher reaction rate than when using $HRh(CO)(PPh_3)_3$, and a linearity of aldehydes up to 99%, were attained. The coordination structure of the effective diphosphines as well as the reasons for the rate enhancement and for the excellent selectivity were discussed.

Industrial hydroformylation processes have been carried out by the use of cobalt or rhodium-complexes as catalysts.[1] Of the two, the latter has been known to be 10^3 times more active than the former.[2] On the other hand, platinum-tin-complex catalysts were investigated by Orchin *et al.*[3] or by Knifton *et al.*[4] with triphenylphosphine as a ligand. They reported that the complex is more active than cobalt-complexes, but far less active than rhodium-complexes, and that, moreover, it gives aldehydes with a high molar ratio of a linear aldehyde to the total aldehydes from a 1-alkene without the addition of any excess of the phosphine. It has also been reported[4] that the activity of the complex was markedly reduced by the addition of 1,2-bis(diphenylphosphino)ethane which can make up a strong chelate ring.

The present authors have found, however, in the course of the study of asymmetric induction in the hydroformylation of butenes using the $PtCl_2((-)$-DIOP)–$SnCl_2$ system,[5] that (−)-DIOP, (4*R*,5*R*)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane, strikingly raises the activity of the platinum-tin system, though it is one of the chelating phosphines. Through a study using $Ph_2P(CH_2)_nPPh_2$,[6] it was revealed that the diphosphine of $n=4$ is particularly effective, while (−)-DIOP is even more so. In this paper, the full details of the study will be described, along with those of further studies undertaken to elucidate the structure of the active catalyst species and the cause of the marked enhancement of the catalytic activity and the selectivity for linear aldehyde.

Experimental

1-Pentene was degassed before use. Thiophene-free benzene was dried over Na and distilled under N_2. The hydrogen was of a pure grade (99.99%), while the CO was of a research grade (99.95%).

The $PtCl_2(PhCN)_2$,[7] (1*R*,2*R*)-1,2-bis(diphenylphosphinomethyl)cyclohexane (II),[8] *trans*-1,2-bis(diphenylphosphinomethyl)cyclopentane (III),[9] (−)-DIOP,[10] (1*S*,2*S*)-1,2-bis(diphenylphosphinomethyl)cyclobutane (IV),[8] *trans*-1,2-bis(diphenylphosphinooxy)cyclopentane (VI),[11] and 1,4-bis(dicyclohexylphosphino)butane (VIII)[12] were prepared according to the literature. The $HRh(CO)(PPh_3)_3$ was purchased (Strem). The (+)-DIOP was presented by Dr. Iwao Ojima, Sagami Chemical Research Center. All the manipurations to prepare phosphines were carried out under N_2.

trans-2,3-Bis(diphenylphosphinomethyl)norbornane(V). To an ether (100 cm^3) suspension of $LiAlH_4$ (7.8 g) was added an ether (800 cm^3) solution of *trans*-5-norbornene-2,3-dicarboxylic acid[13] at a rate to maintain a gentle reflux. After a refluxing for further 40 min, water (7.8 cm^3), 15% NaOH aq. solution (7.8 cm^3) and three portions of water (7.8 $cm^3 \times 3$) were added to the cooled solution succesively. After the decomposition was complete, the solution was filtered to separate the precipitate and was dried over Na_2SO_4; this afforded 10.2 g (98%) of *trans*-5,6-bis(hydroxymethyl)-2-norbornene.

A methanol (100 cm^3) solution of the diol was added to a methanol (10 cm^3) suspension of PtO_2 (0.25 g), and the mixture was stirred under a H_2 atmosphere for 6 h at room temperature until the gas absorption ceased. The filtrate gave *trans*-2,3-bis(hydroxymethyl)norbornane (9.6 g, 93%). The diol was then dissolved in dry pyridine (50 cm^3) and added to a pyridine (110 cm^3) solution of tosyl chloride (35 g) at −20 °C. The solution was stirred for 4 h, while the temperature was allowed to rise to room temperature. The mixture was then poured into 250 cm^3 of ice water, and the colorless precipitate thus formed was separated by filtration and dried *in vacuo*. Recrystallization from MeOH gave 25.8 g (90%) of the ditosylate; mp 101.8—102.8 °C.

The diphosphine was obtained from the ditosylate as a viscous oil according to the procedure in Ref. 8, bp 226—228 °C (bath temperature)/4×10^{-2} Pa, 16.6 g (78%). Found: C, 80.32; H, 7.06%. Calcd for $C_{33}H_{34}P_2$: C, 80.47; H, 6.96%.

*2-*endo*-3-*endo*-2,3-Bis(diphenylphosphinomethyl)norbornane (XI).* 2-*endo*-3-*endo*-2,3-Bis(hydroxymethyl)norbornane[14] (3.1 g) was ditosylated as above and recrystallized from MeOH; 4.6 g (51%). The diphosphine was again prepared according to Ref. 8 as a viscous oil; bp 245—248 °C (bath temperature)/5×10^{-2} Pa, 1.3 g (27%). Found: C, 79.84; H, 6.96%. Calcd for $C_{33}H_{34}P_2$: C, 80.47; H, 6.96%.

cis-1,2-Bis(diphenylphosphinomethyl)cyclohexane (X). X was prepared from the corresponding ditosylate as a viscous oil according to the procedure used for the *trans*-isomer II; bp 215—220 °C (bath temperature)/5×10^{-2} Pa. 65% Yield. Found: C, 79.88; H, 7.15%. Calcd for $C_{32}H_{34}P_2$: C, 79.98; H, 7.13%.

α,α′-Bis(diphenylphosphino)-o-xylene (VII). α,α′-Dibromo-*o*-xylene (Tokyo Kasei)(11 g) was added to a solution of $LiPPh_2$ (prepared from 21.8 g of PPh_3 and 2.6 g of Li in THF (140 cm^3), followed by *t*-BuCl treatment) at 0 °C. After the addition, the mixture was stirred as the temperature rised and refluxed for 30 min. After the solution had cooled, the THF was removed and 40 cm^3 of water was added. The diphosphine was extracted with benzene (100 cm^3, 50 $cm^3 \times$ 2) and recrystallized from EtOH-benzene twice; 13.4 g

(68%); mp 117.0—118.0 °C. Found: C, 81.58; H, 6.08%. Calcd for $C_{32}H_{28}P_2$: C, 81.00; H, 5.95%.

*α,α'-Bis(diphenylphosphino)-*p*-xylene* (IX). IX was prepared as above from α,α'-dibromo-*p*-xylene (6.1 g) and recrystallized from toluene; 5.5 g (50%); mp 177—179 °C. Found: C, 80.92; H, 6.03%. Calcd for $C_{32}H_{28}P_2$: C, 81.00; H, 5.95%.

Hydroformylation Procedure. A typical procedure was as follows: $PtCl_2(PhCN)_2$ 3.2×10^{-5} mol, (−)-DIOP 3.2×10^{-5} mol, and $SnCl_2\cdot2H_2O$ 1.6×10^{-4} mol were placed in a 50 cm^3 Schlenk-tube type high-pressure reactor made of SUS-316, whose inside atmosphere was then replaced by N_2 (99.995%). Benzene (18 cm^3) and 1-pentene (3 cm^3) were added by the use of syringes. Carbon monoxide was pressurrised up to 50 kg/cm^2 (at room temperature); then H_2 (up to 100 kg/cm^2) was added into the reactor, and then heated in a 100 °C oil bath with magnetic stirring. The maximum slope of the pressure-*vs*.-time plot, recorded automatically, was adopted as the measure of the relative rate. The rate in the above reaction when $2PPh_3$ was used in place of (−)-DIOP was taken as the base (100). After the pressure drop had ceased, the reactor was cooled and the residual gas (which was usually about 65 kg/cm^2 at room temperature) was discharged. The reaction solution was then subjected to GLC analysis. Hydrocarbons were analyzed by gas chromatography on a Shimadzu GC-4B apparatus equipped with a column (2 mm i.d.×3 m) of VZ-7 at room temperature. The aldehydes were analyzed on a Shimadzu GC-4A apparatus with a Golay column of DDP-90 at 60 °C.

Results

Catalytic reactions were conducted with the amounts of platinum complexes of 3.2×10^{-5} mol in Figs. 1, 3, and 5, and Tables 2—4, or of 3.2×10^{-6} mol in Figs. 4, 7—13, and Table 1.

Effect of the Structure of Diphosphines. Several α,ω-bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$ ($n=1$—6, 10), were used for activating the $PtCl_2(PhCN)_2$–$SnCl_2\cdot2H_2O$ system as hydroformylation catalysts and compared with PPh_3. The results are presented in Fig. 1. Bis(diphenylphosphino)methane as well as 1,2-bis(diphenylphosphino)ethane were almost completely ineffective. The diphosphine of $n=3$ was equally as effective as PPh_3, and the rate enhancement effect attained maximum at $n=4$, where the reaction rate observed was several times higher than when PPh_3 was used. When *n* exceeded four, the effectiveness was reduced abruptly, and it gradually vanished. The linearity of the aldehydes formed, *i.e.*, the molar ratio of hexanal to the total aldehydes formed (hexanal, 2-methylpentanal, and 2-ethylbutanal) was 91—94%, and it did not greatly depend on the *n* of $Ph_2P(CH_2)_nPPh_2$ except in the case of $n=3$ in which the linearity was reduced to *ca*. 69%. This exceptional linearity at $n=3$ may be caused by the instability of the chelating coordination because of the steric repulsion of 1,3-diaxial phenyl groups of the six-membered chelate ring, which is made up by the coordination of the two phosphorus atoms to the platinum center. A similar exception to the regioselectivity of hydroformylation has been observed in the rhodium-diphosphine-catalyzed reaction of methyl methacrylate or methyl crotonate using $Ph_2P(CH_2)_3PPh_2$.[15]

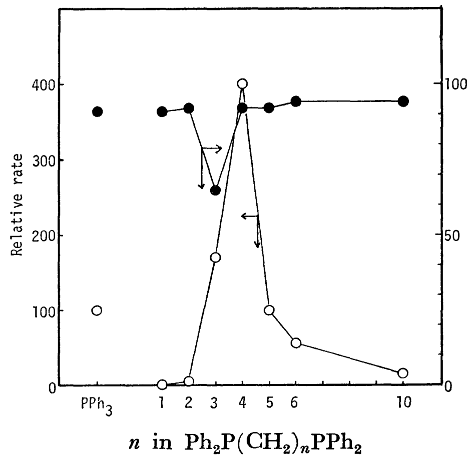


Fig. 1. Effect of methylene chain length of diphosphine ligands in $PtCl_2(PhCN)_2$–$SnCl_2\cdot2H_2O$-catalyzed hydroformylation of 1-pentene.
1-Pentene 3 cm^3, benzene 18 cm^3, $PtCl_2(PhCN)_2$ 3.2×10^{-5} mol, Pt/P/Sn=1/2/5 (atomic ratio), p(CO)=p(H_2)=50 kg/cm^2 initial at room temperature, reaction temperature 100 °C.

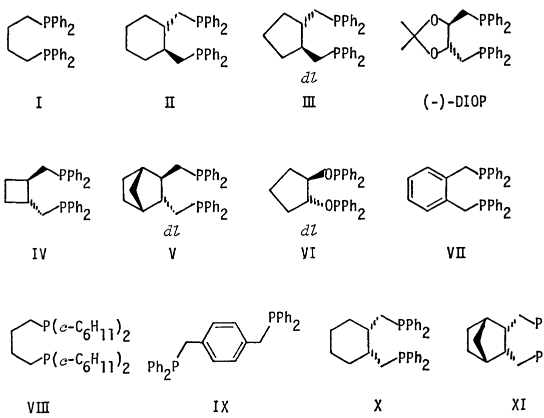


Fig. 2. Bidentate phosphorus ligands used with $PtCl_2(PhCN)_2$–SnX_2 system.

In order to clarify the effect of the structure of the derivatives of 1,4-bis(diphenylphosphino)butane (I) and related compounds on the reaction rate and the product distribution, several diphosphines and phosphorus ligands capable of forming a seven-membered chelate ring like I were prepared and applied to the reactions (Fig. 2). The results are compared with that using the $HRh(CO)(PPh_3)_3$ catalyst. In these reactions, the catalyst concentration was reduced to one-tenth of that in Fig. 1 so that reaction rate could be compared exactly (Table 1).

Under these reaction conditions, the rate-enhancement effect of I (Run 2) was 7.5 times higher than that of PPh_3. It is noteworthy, however, that the reaction time required for complete conversion using I was incomparably shorter than that using PPh_3, because the dependence on the olefin concentration of a reaction rate using a diphosphine was smaller than that of one using PPh_3 as will be discussed later.

The effectiveness of I was further enhanced by bridging the 2- and 3-carbon to construct a rigid and

TABLE 1. EFFECT OF STRUCTURE OF BIDENTATE LIGAND IN THE HYDROFORMYLATION OF 1-PENTENE

Run	Ligand	Time / h	Relative rate[a]	Conversion / %	Product distribution/%[e]		
					Hexanals (Lin.)	Pentane	2-Pentenes
1	$2PPh_3$	24	10	4	79 (92)	8	13
2	I	10	75	100	71 (91)	14	15
3	II	18	60	100	76 (90)	13	10
4	III	4	170	100	73 (96)	9	18
5	(−)-DIOP	5	210	100	75 (96)	9	16
6	*dl*-DIOP	4	240	100	70 (96)	10	20
7	(+)-DIOP	4	240	99	71 (97)	10	19
8	(−)-DIOP[b]	4	210	99	89 (96)	3	8
9	IV	3	310	100	79 (99)	6	13
10	V	2	440	100	72 (99)	8	20
11	Rh[c]	4	240	100	100 (54)	0	0
12	VI	5	180	99	55 (94)	12	33
13	VII	10	80	95	68 (91)	10	22
14	IV[d]	2	400	100	89 (99)	3	8
15	Rh[c,d]	5	120	100	99 (70)	0	1

1-Pentene, 3 cm^3; benzene, 18 cm^3; $PtCl_2(PhCN)_2$, 3.2×10^{-6} mol; $SnCl_2\cdot2H_2O$, 1.6×10^{-5} mol; Pt/P = 1/2 (atomic ratio), $p(CO) = p(H_2) = 50$ kg/cm^2 at room temperature; reaction temperature, 100 °C.

a) The maximum rate of the pressure drop in Run 1 was taken as the base (10). b) $p(CO) = 150$ kg/cm^2. c) Rh: $HRh(CO)(PPh_3)_3$. d) Pt or Rh 3.2×10^{-5} mol, reaction temperature 70 °C. e) The molar ratio of each product. The deficiency was ascribed to some high-boiling product which might be formed through the condensation of aldehydes.

saturated ring skeleton. Both the reaction rate and the product linearity increased distinctly upon the use of *trans*-1,2-bis(diphenylphosphinomethyl)cyclopentane (III) (Run 4), and they increased further upon the use of (1*S*,2*S*)-1,2-bis(diphenylphosphinomethyl)cyclobutane (IV) with a saturated four-membered ring (Run 9). The effectiveness of (1*R*,2*R*)-1,2-bis(diphenylphosphinomethyl)cyclohexane (II) as a ligand (Run 3) was almost identical with that of I; that is, the attempt at the construction of a flexible six-membered ring skeleton was ineffective. The higher effectiveness of (−)-DIOP (Run 5) than that of III (Run 4) may be due to the somewhat smaller size of the dioxolane ring than that of the cyclopentane ring.

These diphosphines, however, accelerated not only the hydroformylation reaction, but also such side reactions as the hydrogenation[16] and isomerization of the olefin. Of course, the side reactions could be diminished by raising the carbon monoxide partial pressure, as is shown by the comparison of Runs 5 and 8. Even in this case, however, the reaction rate was not sacrificed because of the nearly zero-order rate dependence on the pressure, which will be discussed later. By the use of IV, which has a more rigid ring skeleton, the relative rate was increased 31 times in comparison with that when PPh_3 was used, and the product linearity was raised up to 99%. The reaction rate observed using IV was apparently higher than that in the reaction catalyzed by $HRh(CO)(PPh_3)_3$ in the absence of excess PPh_3 (Run 11). The superiority of the $PtCl_2$–IV–$SnCl_2\cdot2H_2O$ system to $HRh(CO)(PPh_3)_3$ was distinctly shown in the reactions with higher catalyst concentrations at the lower reaction temperature of 70 °C (Runs 14 and 15).

A bicyclic diphosphine, *trans*-2,3-bis(diphenylphosphinomethyl)norbornane (V) (Run 10), showed the highest effectiveness as a catalyst ligand; the observed relative rate was 44 times higher than that observed using PPh_3.

As has been shown by Knifton *et al.*[4] with various monodentate ligands, such as PPh_3 or $P(n\text{-}Bu)_3$, the electronic effect of phosphines did not influence the result in Pt-Sn catalyzed hydroformylation very much. This was fairly true for bidentate ligands; *trans*-1,2-bis(diphenylphosphinooxy)cyclopentane VI (Run 12) and III (Run 4), which are sterically similar but electronically different, gave similar results. Further, α,α′-bis(diphenylphosphino)-*o*-xylene VII (Run 13), which must be electronically different from II, caused an activity similar to that caused by II. Thus, the effectiveness of diphosphines as catalyst ligands is considered to be determined mainly by a steric factor. However, the difference in electron-donating ability between a diarylphosphino group and a dialkylphosphino one may be multiplied when they are in bidentate ligand. In fact, 1,4-bis(dicyclohexylphosphino)butane (VIII) (Table 2) was far less effective than I, and also less effective than the monodentate ligand PPh_3, probably because its donating ability is too high.

In order to elucidate the further steric requirements, closely related isomers of diphosphines were prepared and their degrees of effectiveness were compared. The catalyst-system concentration was the same as in Fig. 1 (Table 2). α,α′-Bis(diphenylphosphino)-*p*-xylene (IX), which is unable to effect chelation, was distinctly less effective than the position isomer, VII, and also

Table 2. Effect of structure of diphosphine in the $PtCl_2(PhCN)_2$-diphosphine-$SnCl_2 \cdot 2H_2O$-catalyzed hydroformylation of 1-pentene

Diphosphine	Time / h	Relative rate	Conversion / %	Product distribution/% Hexanals (Lin.)	Pentane	2-Pentenes
I	1.5	400	100	74(92)	12	14
VIII	17	50	76	63(91)	5	25
VII	2	370	100	64(87)	11	25
IX	6	80	94	62(85)	5	33
II	2	340	100	69(92)	11	14
X	2.5	180	100	71(90)	8	21
V	1	1880	100	53(97)	9	14
XI	1	720	100	42(92)	8	22
PPh_3	5	100	87	84(91)	5	11
PPh_3[a]	3.5	180	100	58(86)	7	17
PPh_2Et	4	150	100	79(89)	7	15
PPh_2Et[a]	4	120	100	62(86)	7	19

1-Pentene, 3 cm^3; benzene, 18 cm^3; Pt 3.2×10^{-5} mol; Pt/P/Sn=1/2/5 (atomic ratio); p(CO)=p(H_2)=50 kg/cm^2 at room temperature; reaction temperature, 100 °C.

a) Pt/P/Sn=1/1/5.

less effective than monophosphines. On the other hand, among the stereo isomers of 1,2-bis(diphenylphosphinomethyl)cyclohexanes (II and the *cis*-isomer X) and 2,3-bis(diphenylphosphinomethel)norbornane (V and the *endo*, *endo*-isomer XI), *cis*-isomers were half as effective as the corresponding *trans*-isomers. That is, a *trans*-configuration of the ring skeleton of the diphosphines was more favorable to rate enhancement than a *cis*-configuration, although the former seems to be fairly disadvantageous to chelating coordination.

Effect of P/Pt Atomic Ratio. It is well known that the amount of excess phosphine plays a significant role in the activity and selectivity of rhodium catalysts in hydroformylation.[17] However, in the $PtCl_2$-$SnCl_2$ catalyzed hydroformylation,[4] it was reported only that excess PPh_3 retarded the reaction, even at P/Pt=4. In contrast with this, the effect of the P/Pt ratio of diphosphines on the reaction rate was more serious than has been expected, as is shown in Fig. 3. That is, the optimum P/Pt ratio to attain the maximum reaction rate was between 1.0 and 2.0, but not so distinct when a monophosphine such as PPh_3 or PPh_2Et was used. In contrast, when diphosphine I was used, the optimum P/Pt value increased to 2.0 and became distinct. By the use of a more effective diphosphine, (−)-DIOP, this value became about 2.5—3.0. That is, the more effective the ligand, the higher the optimum P/Pt atomic ratio.

By the use of the most effective ligand, V, the effect of the P/Pt ratio was investigated with a catalyst amount one-tenth of that in Fig. 3. At this concentration, the optimum ratio of (−)-DIOP increased somewhat to about 3 as is shown in Fig. 4, while the reaction rate obtained by the use of V showed a plateau between 2.0—3.5 values of the P/Pt ratio.

Effect of Tin (II) Halide. It has been reported that the effectiveness of tin(II) halide as a cocatalyst for $PtCl_2(PPh_3)_2$ was in the order of $SnCl_2 \cdot 2H_2O$>

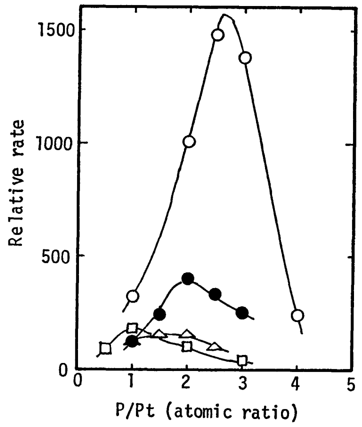


Fig. 3. Effect of phosphorus to platinum ratio in hydroformylation of 1-pentene catalyzed by $PtCl_2(PhCN)_2$-phosphine-$SnCl_2 \cdot 2H_2O$ system.
Reaction conditions are the same as in Fig. 1 except phosphine amount. ○: (−)-DIOP, ●: I △: PPh_2Et, □: PPh_3.

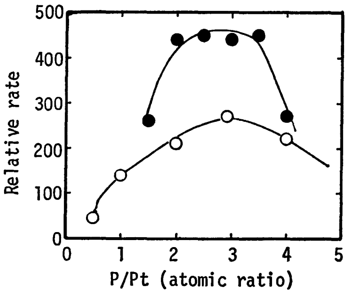


Fig. 4. Effect of phosphorus to platinum ratio in hydroformylation of 1-pentene catalyzed by $PtCl_2(PhCN)_2$-diphosphine-$SnCl_2 \cdot 2H_2O$ system.
Reaction conditions are the same as in Table 1 except phosphine amount. ●: V, ○: (−)-DIOP.

Table 3. Effect of the sort of stannous halide in the $PtCl_2(PhCN)_2$-phosphine-SnX_2-catalyzed hydroformylation of 1-pentene

Phosphine	SnX_2	Time/h	Relative rate	Conversion/%	Product distribution/%		
					Hexanals (Lin.)	Pentane	2-Pentenes
$2PPh_3$	SnF_2	24	25	61	87(95)	5	8
	$SnCl_2\cdot 2H_2O$	5	100	87	84(91)	5	11
	$SnBr_2$	5	65	98	76(92)	5	19
	SnI_2	24	5	26	85(90)	4	11
(−)-DIOP	SnF_2	1.5	1180	100	75(94)	9	15
	$SnCl_2\cdot 2H_2O$	1	1010	100	75(95)	10	15
	$SnCl_2$	0.5	1140	100	77(96)	8	15
	$SnBr_2$	1	620	100	55(96)	10	25
	SnI_2	8	45	100	64(93)	8	28

The reaction conditions are the same as in Table 2.

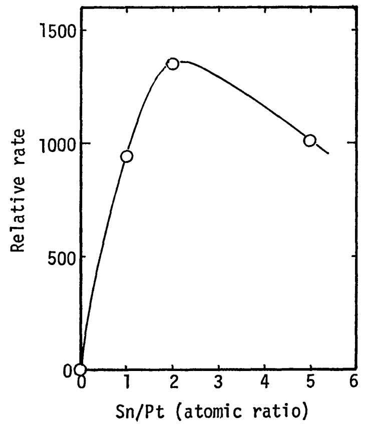


Fig. 5. Effect of tin to platinum ratio in $PtCl_2(PhCN)_2$-(−)-DIOP-$SnCl_2\cdot 2H_2O$-catalyzed hydroformylation of 1-pentene.
Reaction conditions are the same as in Fig. 1 except $SnCl_2\cdot 2H_2O$ amount.

Table 4. Relative rate in the hydroformylation of 1-pentene catalyzed by $PtCl_2(PhCN)_2$-(−)-DIOP-$SnCl_2\cdot 2H_2O$ in various solvents

Solvent	Relative rate
Benzene	1010
CH_2Cl_2	920
Acetone	350
THF	170
CH_3CN	130
Hexane	45
MeOH	5

The reaction conditions are the same as in Table 2 except for the solvent.

$SnBr_2 > SnI_2$.[4] Tin(II) fluoride, which had not yet been used, was less effective than bromide (Table 3). However, the fluoride was more effective than $SnBr_2$, and as effective as $SnCl_2\cdot 2H_2O$, when a diphosphine, (—)-DIOP, was used. Although it is uncertain how much SnX_2 operates as an anionic ligand, SnX_2Cl, as in the case of $SnCl_2$,[18] these results indicated that the effect of a cocatalyst was different depending on whether a phosphorus ligand was monodentate or bidentate.

The effect of the Sn/Pt atomic ratio was examined by the use of the most effective $SnCl_2\cdot 2H_2O$ as a cocatalyst for $PtCl_2$-(—)-DIOP-system; the results are shown in Fig. 5. The system had no activity without tin(II) halide, and the significant activity appeared even at Sn/Pt=1, which suggests that one $SnCl_3$ group is necessary for, and also enough for the catalytically active species.

Choice of Solvent. The effect of the solvent on the reaction rate using the $PtCl_2$–diphosphine–$SnCl_2$ system was examined, the results are listed in Table 4. The relative rate was the highest when benzene or CH_2Cl_2 was used. In the latter, however, the linearity was low (89%), and, after the reaction, some metal deposit was observed. Acetone, which was one of the best solvents for the $PtCl_2(PPh_3)_2$–$SnCl_2$ system,[4] was not so suitable for the diphosphine system. Thus, it was best to carry out the reaction in benzene when diphosphines were used.

Effect of Reaction Variables. A diphosphine must coordinate to a platinum-metal center competing with olefin, hydrogen, and carbon monoxide. Therefore, the behavior of a diphosphine can be clarified if the effect of the catalyst or olefin concentration and the H_2 and CO partial pressure are examined. Thus, these variables were altered by the use of (—)-DIOP and benzene as diphosphine and solvent respectively, and the relative rate was measured.

The relative rate was plotted full-logarithmically against the charged amount of the catalyst system. The slope means that the order to the catalyst concentration was about 0.7 (Fig. 6)

On the other hand, the relation between the initial olefin concentration and relative rate (Fig. 7) showed the order of *ca.* 0.3, which was remarkably low for the dependence on the olefin concentration in hydroformylation. Hence, the reaction rate was nearly constant until almost all the olefin had been consumed, and the total reaction time required for a complete conversion was remarkably shorter than would be expected from the relative rate comparison between

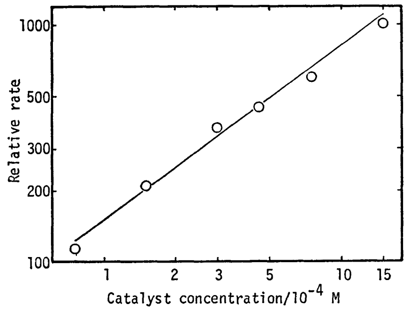


Fig. 6. Full-log plot of relative rate *vs.* catalyst system concentration in $PtCl_2(PhCN)_2$–(−)-DIOP–$SnCl_2 \cdot 2H_2O$-catalyzed hydroformylation of 1-pentene.
Reaction conditions are the same as in Table 1 except catalyst system concentration.

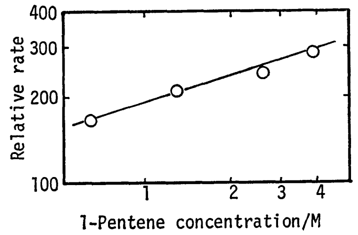


Fig. 7. Full-log plot of relative rate *vs.* 1-pentene concentration in $PtCl_2(PhCN)_2$–(−)-DIOP–$SnCl_2 \cdot 2H_2O$ catalyzed hydroformylation of 1-pentene.
Reaction conditions are the same as in Table 1 except 1-pentene concentration.

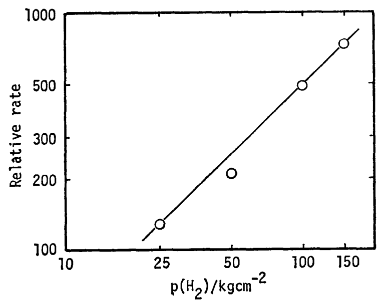


Fig. 8. Full-log plot of relative rate *vs.* $p(H_2)$ (initial at room temperature) in $PtCl_2(PhCN)_2$–(−)-DIOP–$SnCl_2 \cdot 2H_2O$-catalyzed hydroformylation of 1-pentene. Reaction conditions are the same as in Table 1 except $p(H_2)$.

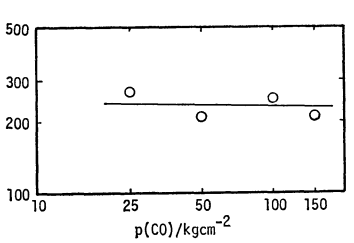


Fig. 9. Full-log plot of relative rate *vs.* p(CO) (initial at room temperature) in $PtCl_2(PhCN)_2$–(−)-DIOP–$SnCl_2 \cdot 2H_2O$-catalyzed hydroformylation of 1-pentene. Reaction conditions are the same as in Table 1 except p(CO).

the case of (−)-DIOP and that of PPh_3.

The rate was proportional to the H_2 partial pressure, $p(H_2)$ (Fig. 8). The reaction order was almost 1.0 with respect to $p(H_2)$, as in other hydroformylation catalyst systems. On the other hand, the rate hardly depended on p(CO) at all, and Fig. 9 indicates an order of nearly zero.

The product distribution virtually did not depend at all on the reaction variables except on the partial pressures of CO and H_2. Isomerization was suppressed by increasing $p(H_2)$ or p(CO), while hydrogenation was suppressed by increasing p(CO) or decreasing $p(H_2)$.

Although the kinetic order described above was rather qualitative, the results can be represented by the following rate expression in the range of the abovementioned reaction conditions:

$$\text{Rate} \propto [\text{Pt}]^{0.7}[\text{1-Pentene}]^{0.3}p(H_2)^{1.0}p(\text{CO})^{0.0}. \quad (1)$$

Effect of the Structure of Olefins. In the previous sections, 1-pentene has been used as the substrate because it is easy to handle and also easy to analyze the isomerization or hydrogenation products. The present catalyst system was further applied to propene or 1-butene hydroformylation, and the results were compared with that of 1-pentene. As is shown in Fig. 10, the shorter a 1-alkene was, the lower the product linearity. However, the effect of the rigid ring skeleton of a diphosphine on the linearity became distinct with shorter olefins.

Internal olefins reacted only sluggishly. For example, the rate of *cis*-2-pentene hydroformylation was one twentieth that of 1-pentene, and the product was composed of aldehydes (linearity 65%) 43%, *trans*-2-pentene 38%, *cis*-2-pentene 11%, and pentane 4%.

Effect of Temperature. The hydroformylation of propene was carried out at various temperatures between 80—140 °C by the use of the $PtCl_2$–IV–$5SnCl_2 \cdot 2H_2O$ catalyst system (Fig. 11). Lowering the reaction temperature improved the yield of aldehydes, which means the competitive hydrogenation or aldehyde loss was almost entirely suppressed. The linearity in aldehydes was also improved by lowering the temperature.

Effect of Total Pressure. It is important, from the industrial point of view to know to what degree

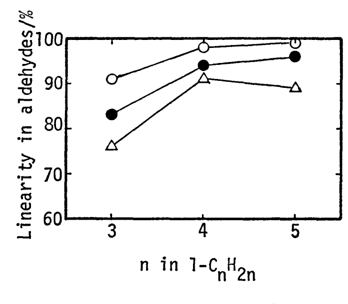


Fig. 10. Effect of the structure of diphosphines and the chain length of 1-alkene on the selectivity to the straight-chain aldehyde.
Other conditions are the same as in Table 1. ○: IV, ●: (−)-DIOP, △: II.

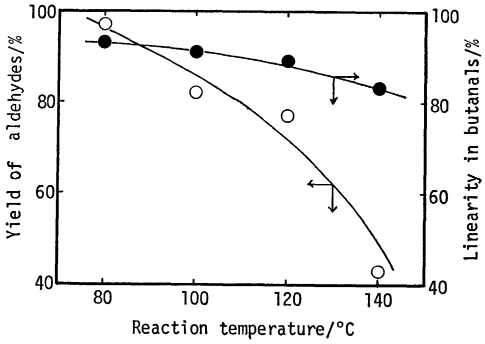


Fig. 11. Effect of reaction temperature in the hydroformylation of propene catalyzed by $PtCl_2(PhCN)_2$–IV–$SnCl_2 \cdot 2H_2O$-system.

Propene(*l*) 3 cm^3, other conditions are the same as in Table 1 except reaction temperature.

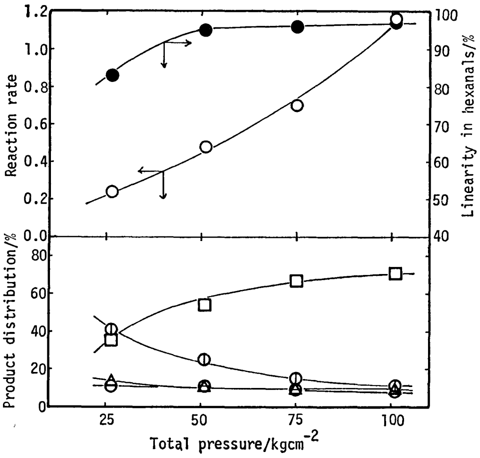


Fig. 12. Effect of total pressure ($CO/H_2=1$) on the product distribution, linearity in the aldehydes, and reaction rate in $PtCl_2(PhCN)_2$–(−)-DIOP–$SnCl_2 \cdot 2H_2O$-catalyzed hydroformylation of 1-pentene at constant pressure.

Reaction conditions are the same as in Table 1 except gas pressures. □: Hexanals, △: pentane, ⦶: *trans*-2-pentene, ⊖: *cis*-2-pentene.

the total gas pressure can be lowered. Thus, 1-pentene was hydroformylated by the use of $PtCl_2(PhCN)_2$–[(−)-DIOP]–$SnCl_2 \cdot 2H_2O$ (Pt/P/Sn=1/2/5, atomic ratio) at a constant pressure (Fig. 12). Lowering the pressure decreased the relative rate, as was expected from the effect of partial pressures shown in Figs. 8 and 9. Aldehyde linearity was almost constant down to a pressure of 50 kg/cm^2, but it was lowered gradually below that pressure. The product distribution showed an interesting pattern; with a lowering of the total pressure, the yield of aldehydes was decreased until *ca.* 35% at 25 kg/cm^2, while those of *cis*-2-pentene and pentane remained almost constant, and only that of *trans*-2-pentene increased.

Also, in the reaction of propene carried out by the use of the most active catalyst system, $PtCl_2(PhCN)_2$–V–$SnCl_2 \cdot 2H_2O$, at the optimum atomic ratio of Pt/P/Sn (1/3/2.5) (Fig. 13), the relative rate decreased with a lowering of the pressure, as above. On the other hand, the yield of aldehydes and its

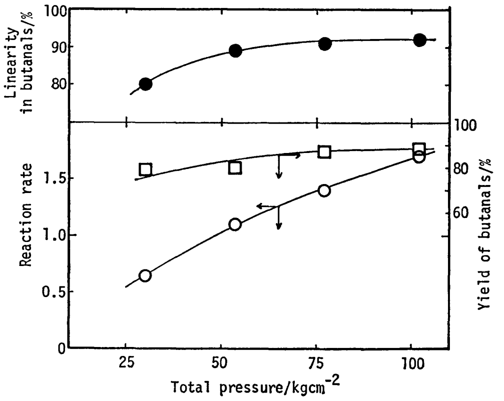


Fig. 13. Effect of total pressure ($CO/H_2=1$) on $PtCl_2(PhCN)_2$–V–$SnCl_2 \cdot 2H_2O$ catalyzed hydroformylation of propene at constant pressure.

Propene(*l*) 3 cm^3, Pt/P/Sn=1/3/2.5, other conditions are the same as in Table 1 except gas pressures.

linearity was not so much lowered, because the isomerization of the olefin is excluded; *i.e.*, even at a total gas pressure of 25 kg/cm^2, both values were more than 80%.

Discussion

The rate-enhancement effect of diphosphines in hydroformylation has been observed in the rhodium-catalyzed reaction of 1-alkenes by the use of $Ph_2P(CH_2)_nPPh_2$ (n=2—4)[19] or IV.[20] However, the degree of the enhancement was low, *i.e.*, two times at the most. These effects can be interpreted as showing that a little excess of diphosphine plays the role of a large excess of monophosphine in keeping the rhodium complex catalytically active by coordination. The effect became more distinct in the rhodium-catalyzed hydroformylation of ethyl acrylate.[15] However, the operating mechanism of diphosphines in the rate enhancement seems to be qualitatively different from that of the platinum–diphosphine-catalyzed hydroformylation presented in this paper, because, in the rhodium-catalyzed reaction, $Ph_2P(CH_2)_nPPh_2$ are effective only for ethyl acrylate, and the diphosphines of n=2 and 3, which were ineffective in the platinum-catalyzed reaction, also accelerated this reaction.

Figure 14 shows the conceivable coordination types of diphosphines in square-planar platinum complexes. Among these, **A** was postulated for the $PtCl(SnCl_3)$-[(−)-DIOP] complex.[21] A complex of the **B** type was prepared with $(t\text{-Bu})_2P(CH_2)_nP(t\text{-Bu})_2$, $n \geqq 9$.[22] A di- or trinuclear complex of the **C** or **D** type was isolated by the use of $Ph_2P(CH_2)_nPPh_2$ of n=3 or 4 respectively.[23]

As has been reported in Ref. 4, 1,2-bis(diphenylphosphino)ethane, which is known to form a complex of the **A** type, inhibited the reaction almost completely. Moreover, $Ph_2PCH_2PPh_2$ was also completely ineffective (Fig. 1), and the recovered precipitate in the reaction solution showed a ^{31}P NMR spectrum which was ascribable to a chelating form rather than a bridged one.[24] However, many results in this paper support the idea that the active species has a form

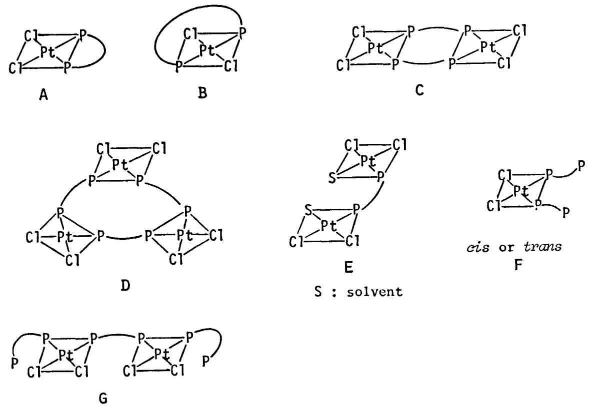


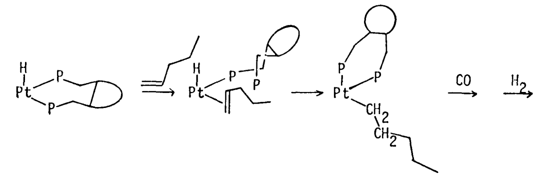
Fig. 14. Conceivable coordination types of diphosphines in square planar platinum complexes.

of the **A** type, where the chelating coordination is rather loose. In $Ph_2P(CH_2)_nPPh_2$ (n=1—10), only that of n=4 was prominent as a catalyst ligand (Fig. 1), and so the possibility of **B**-type coordination can be excluded. On the other hand, the possibility that a diphosphine bridges two platinum centers in the active species is negligible judging from the following considerations: 1) If the active species is a di- or trinuclear complex of the **C** or **D** type, with two or three bridging diphosphine molecules, the result of the reaction by the use of the *dl*-form of a diphosphine would be different from the result when only one antipode of the diphosphine is used, because the former might give a complex which has both antipodes. However, the result using *dl*-DIOP was almost the same as that when (−)-DIOP or (+)-one was used. 2) An α,α'-bis(diphenylphosphino)-*p*-xylene, IX, which is able to make only a bridging coordination, was much less effective than the *o*-isomer, VII, which is electronically similar to IX but which is able to form a *cis*-chelation complex of the **A** type. 3) The reaction rate depended on the charged-catalyst amount in the order of *ca.* 0.7 (Fig. 6), which may be due to the aggregation of the active species of the **A** type by the formation of inactive bridging complexes, such as **C** or **D**, with an increase in the catalyst concentration. Thus, the bridging-type coordination of **C** and **D** can be excluded.

As is shown in Fig. 3, the effectiveness of diphosphines I and (−)-DIOP was extremely low at the P/Pt atomic ratio of 1, in contrast with the inefficiency at P/Pt=2, and there was no significant difference either in rate enhancement or in product linearity between diphosphines and monophosphines so long as the P/Pt ratio in the reaction system was 1. This result suggests that, even if another bridging complex of the **E** type is formed at P/Pt=1, it operates as if it were a monophosphine complex of P/Pt=1. On the other hand, the presence of excess diphosphine retarded the reaction distinctly; the relative rate at P/Pt=4 was similar to that using PPh_2Et at P/Pt=2, probably because the diphosphines at a high P/Pt ratio behave as monodentate ligands, as in Type **F** or **G**.

Rather high optimum ratios of P/Pt of *ca.* 3 was observed for diphosphines with a rigid ring skeleton, as is shown in Figs. 3 and 4. This may be explained as follows. Because of the steric rigidity, it is difficult for these diphosphines to make a *cis*-chelating coordination. Therefore, not enough of the catalytically active species of Type **A** is formed at P/Pt up to 2, while some bridged complexes, such as **C** and **D**, may be formed. When excess diphosphine is added, it may displace one phosphorus end of bridging diphosphine in, for example, **C** to make up a bridging complex such as **G**, whose P/Pt ratio is 3. This dinuclear complex then dissociates to give the active species, **A**, and the inactive complex, **F**. Thus, some excess of diphosphine is necessary to maximize the concentration of the active species, **A**.

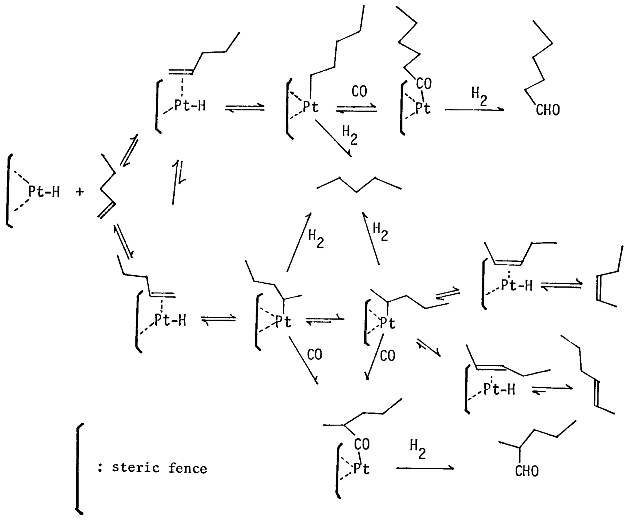
On the other hand, the ineffectiveness of 1,2-bis(diphenylphosphino)ethane and 1,4-bis(dicyclohexylphosphino)butane indicates the necessity of the dissociation of a chelating diphosphine during the catalytic cycle. The necessity of the loose *cis*-chelation of a diphosphine can be explained as follows. In contrast with a rhodium or cobalt system, $SnCl_3$ is necessary as a supplementary ligand, and it is considered to occupy one coordination site throughout the catalytic cycle; moreover, one phosphorus atom, probably trans to $SnCl_3$, has to dissociate to provide a vacant site for the activation of olefin, CO, and H_2. As Pt–P bonds are comparatively stable,[25] the dissociation can not easily occur without the aid of the instability of a seven-membered chelate ring, which is increased by the construction of a rigid ring skeleton.



Scheme 1.

As is shown in Scheme 1, the reaction site for olefin is provided by the dissociation of one phosphorus end of the diphosphine, and the following *cis*-addition of H–Pt to the C=C bond of the olefin to give the σ-alkyl complex may be accelerated[26] by the recoordination of the dissociated phosphorus end, which is forced to be located near the reaction site by the steric bulkiness of the rigid ring skeleton of the diphosphine itself. This process may operate in successive steps of CO insertion and/or hydrogenolysis. In this manner, 1,4-bis(diphenylphosphino)butane derivatives can enhance the hydroformylation as well as competitive hydrogenation. On the other hand, the hydroformylation catalyzed by the $PtCl_2$–diphosphine–$SnCl_2\cdot 2H_2O$ system showed a low-order dependence of the rate on the CO partial pressure and on the olefin concentration in comparison with the reactions catalyzed by the $PtCl_2(PPh_3)_2$–$SnCl_2\cdot 2H_2O$ system,[4] $Co_2(CO)_8$,[27] and $Rh_4(CO)_{12}$[28] where the rate expressions were proportional to $[Pt]^{1.5}[Olefin]^{1.0}p(H_2)^{1.0}\cdot p(CO)^{-0.5}$, $p(H_2)/[p(H_2)+p(CO)]\times[Co][Olefin]$, and $[Rh][Olefin]p(H_2)/p(CO)$ respectively. The low dependence of the rate on [Olefin] suggests a spontaneous dissociation of one phosphorus end of the chelated diphosphine, affording a vacant site. The low dependence on the CO partial pressure also suggests that the diphosphine keeps off the excess coordination of CO, which retards the reaction. However, the first-order dependence of the reaction rate on p(H_2) is like that in a rhodium- or cobalt-catalyzed reaction, in which the rate-determining step is considered to be the hydrogenolysis of an acyl complex.

Not only the remarkable rate enhancement, but also the improvement of linearity in aldehydes produced was brought about by diphosphines bearing rigid ring skeletons. The linearity is originally as high as 92% (Table 1), even when the $PtCl_2(PPh_3)_2$–$SnCl_2 \cdot 2H_2O$ catalyst was used, much higher than when the $HRh(CO)(PPh_3)_3$ or cobalt catalyst was used, this difference may be ascribed to both the steric bulkiness of the $SnCl_3$ ligand and that of the two PPh_3 ones, which do not easily dissociate. The rigidity and bulkiness of the ring skeletons of diphosphines must cause a larger steric hindrance, not only when the diphosphine makes a *cis*-chelating coordination, but also when its one phosphorus end dissociates in order to receive substrate or reactant molecules.



Scheme 2.

The process of how a terminal olefin gives linear aldehyde is shown schematically in Scheme 2. The increase in isomerized *trans*-2-pentene in comparison with *cis*-pentene with a prolonged reaction time can also be explained by the scheme. The steric hindrance is considered to prevent *trans*-2-pentene from taking part in the catalytic cycle again.

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