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Catalytic Oligomerization of Isoprene in Solution. Coordination Features of Phosphorus Ligands in the Ni (0) Complexes

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Dedicated to Professor Otohiko Tsuge on the occasion of his retirement

The oligomerization of isoprene in HMPA catalyzed by NiCl_2L_2 (L: phosphorus ligands)- NaBH_4 has been kinetically investigated by varying the kind and amounts of phosphorus ligands and the amounts of NaBH_4 . Triphenylphosphine (PPh_3), which formed the most active catalyst, is removed from the coordination sphere of the complex under the high isoprene-concentration, giving a negative reaction order in isoprene. In contrast, alkyl phosphines, the better coordinating ligands, give zero order kinetics, although the intrinsic activities of their complexes are rather limited. A small excess of triphenylphosphine in the reaction medium changes the order to zero, allowing the highest activity even in a high isoprene/Ni ratio beyond 1000.

The reaction mechanism, the selectivity, and the activity order of phosphorus ligands are discussed, assuming that the elimination of the oligomeric product is rate-determining.

Catalytic dimerization reactions of conjugated dienes have been intensively studied since the pioneer work of Wilke group^{1,2)} using various systems that contain nickel ion of various coordination structures, however their practical application is rather limited because of their insufficient catalytic activity, selectivity, and life-time, especially for isoprene. An exception is the excellent activity of $\text{Fe}(\text{acac})_3\text{-AlEt}_3$ -Schiff-base catalyst.³⁾ The present authors have reported the enhanced activity of the $\text{NiCl}_2(\text{PPh}_3)_2\text{-NaBH}_4$ catalyst system by the addition of amine in the presence of suitable amounts of water using benzene as the solvent.^{4a, b)} However, the total catalytic turnover number was still very limited, so that the complete conversion of isoprene could never be achieved when the mole ratio of substrate charged to the catalyst was over only 100. Total catalytic turnover number as well as activity were found recently to be improved to a significant extent in some aprotic polar solvents such as hexamethylphosphorotriamide (HMPA), where the number could be beyond 1000.^{4c)}

In the present study, the catalysis in HMPA was further investigated from the kinetic

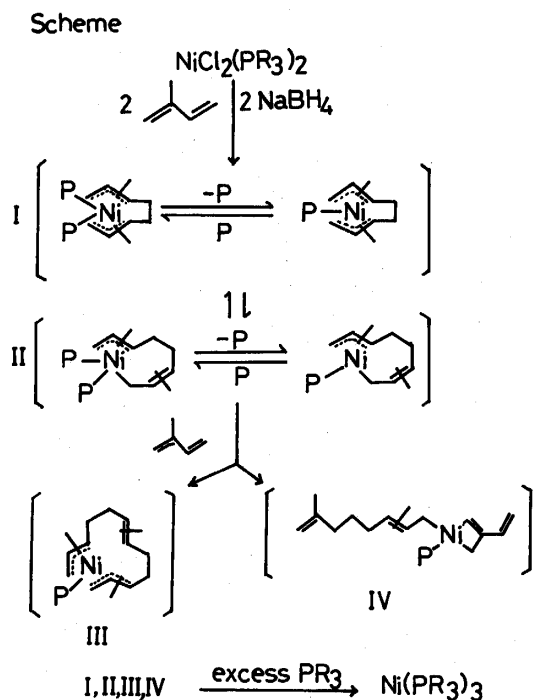
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viewpoint in order to find ways to enhance the reaction rate to a practical level. The effects of type and amounts of phosphorus ligands in the catalytic system on the catalytic activity were emphasized, since Wilke et al.²⁾ reported that the activity was highest when one molecule of phosphorus ligand was coordinated to the catalyst complex. Tolman's conclusion on the electronic and steric characteristics of a series of ligands⁵⁾ may be another clue to the present approach. Some mechanistic details of the catalytic oligomerization could be discussed based on such results.

Experimental

$\text{NiCl}_2(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PPh}_3$, ethyldiphenylphosphine (PEtPh_2), methyldiphenylphosphine (PMePh_2), diethylphenylphosphine (PEt_2Ph), dimethylphenylphosphine (PMe_2Ph), triethylphosphine (PEt_3), trimethylphosphine (PMe_3)) was prepared according to the method described in the literatures.⁶⁻⁹⁾

All organic reagents were purified by distillation under nitrogen atmosphere. The oligomerization reaction was carried out in a sealed glass tube which was kept in an oil bath heated at 80°C . The standard reaction components consisted of 0.2mmol NiCl_2L_2 , 0.6 or 2mmol NaBH_4 , 1ml hexane (the internal standard), 4.7ml HMPA and 4.8ml isoprene (the molar ratio of isoprene/Ni was 240 in this case). After the contents were frozen in liquid nitrogen, the tube was degassed in vacuo to be sealed. After the reaction was over, the reaction mixture was washed with 1N HCl (to remove HMPA and the catalyst) and then the mixture of isoprene oligomers and the internal standard was analyzed by a gas-chromatograph (Yanagimoto Co.



G2800) using a column packed with Apiezon Grease L.

The oligomeric products in the present study were dimethyloctadienes (2,6-and 2,7-dimethyl-2,6-octadienes and 2,6-dimethyl-1,6-octadiene) (DMOD), 2,6-dimethyl-1,3,6-octatriene (DMOT), dipentene (1,8(9)-p-methadiene) (DP), 1,5- and 2,5-dimethyl-1,5-cyclooctadienes (DMCOD), 1,5,9-trimethyl-1,5,9-cyclododecatriene (TMCDT), 1,6,11-trimethyl-1,6,11-dodecatetraene (TMDT) and tetramers. Oligomers other than tetramers were identified in previous papers.^{2,3)} The tetramers were estimated in a gas-chromatogram with authentic samples without detailed structural analysis.

³¹P{¹H}-NMR spectra were measured with an FT-NMR spectrometer (JEOL, JNE-FX100) at 40.32 MHz using 85% H₃PO₄ as an external reference. The samples of NiCl₂(PR₃)₂-NaBH₄ system were prepared from 0.5mmol NiCl₂(PR₃)₂, 1.5 or 5mmol NaBH₄, 10mmol (1ml) isoprene and 1.5ml (80mmol) dimethylacetamide. After 30 minutes' reaction at 80°C, ³¹P{¹H}-NMR spectra were measured at 60°C.

Results and Discussion

Catalytic Activities of NiCl₂(PR₃)₂-NaBH₄ System for the Oligomerization of Isoprene.

Catalytic activities of NiCl₂(PR₃)₂-NaBH₄ with the system at an isoprene/Ni ratio of 240 (NaBH₄/Ni ratio is either 3 or 10) are summarized in Tables 1 and 2. The conversion strongly depends on the kind of phosphorus ligand as well as the amounts of NaBH₄. When the NaBH₄/Ni ratio is fixed at 3, the catalytic activity of the phosphorus complex catalysts decreases in the order PMePH₂ ≈ PEtPh₂ > PMe₂Ph > PPh₃ >> PMe₃ ≈ PEt₂Ph > PEt₃ (Table 1). In contrast,

Table 1. Effects of phosphorus ligands on the oligomerization of isoprene.^{a)}

Ligand	Conv (%)	Yield (%)								
		DMOD	DMOT	DP	DMCOD	TMDT	TMCDT	Other trimers	Tetramers	Others
PPh ₃	85.0	1.1 (1.3)	5.4 (6.4)	8.4 (9.9)	26.3 (30.9)	14.8 (17.4)	13.7 (16.1)	3.3 (3.9)	12.1 (14.2)	—
PEt ₃	50.0	0.7 (1.3)	3.3 (6.5)	6.8 (13.5)	4.2 (8.3)	13.1 (26.2)	11.5 (21.0)	5.3 (10.6)	5.2 (10.4)	1.1 (2.1)
PMe ₃	64.6	0.8 (1.2)	3.6 (5.6)	10.1 (15.7)	4.8 (7.5)	11.2 (17.3)	20.7 (32.0)	3.8 (5.9)	7.9 (12.3)	1.7 (2.7)
PEt ₂ Ph	55.0	1.3 (2.4)	3.7 (6.7)	9.6 (17.5)	5.6 (10.1)	4.3 (7.9)	16.9 (30.8)	0.4 (0.8)	5.5 (10.0)	7.6 (13.8)
PMe ₂ Ph	74.2	0.4 (0.5)	5.5 (7.4)	14.0 (18.9)	7.0 (9.5)	14.6 (19.7)	19.5 (26.3)	2.4 (3.3)	10.7 (14.4)	—
PEtPh ₂	96.7	0.6 (0.6)	8.1 (8.4)	23.3 (24.1)	20.6 (21.3)	15.0 (15.5)	12.3 (12.7)	1.7 (1.8)	15.2 (15.7)	—
PMePh ₂	92.9	0.3 (0.3)	5.3 (5.7)	20.0 (21.6)	19.3 (20.8)	10.5 (11.3)	21.0 (22.6)	1.3 (1.4)	13.2 (14.2)	2.0 (2.1)

a) NiCl₂(PR₃)₂ : 0.2 mmol; NaBH₄ : 0.6 mmol; isoprene : 4.8 ml; HMPA : 1.7 ml; reaction temperature : 80°C; reaction time : 24 h; numbers in parenthesis are selectivities.

Catalytic Oligomerization of Isoprene

Table 2. Effects of phosphorus ligands on the oligomerization of isoprene.^{a)}

Ligand	Conv (%)	Yield (%)								
		DMOD	DMOT	DP	DMCOD	TMDT	TMCDT	Other trimers	Tetra-mers	Others
PPh ₃	97.9	1.8 (1.8)	22.4 (22.9)	27.3 (27.9)	15.2 (15.5)	6.6 (6.7)	6.8 (6.8)	0.8 (0.8)	15.9 (16.2)	1.3 (1.3)
PEt ₃	29.2	0.8 (2.6)	2.7 (9.3)	5.4 (18.6)	2.6 (6.7)	—	4.4 (15.1)	6.2 (21.3)	7.3 (24.9)	0.4 (1.3)
PMe ₃	27.1	1.6 (6.0)	3.5 (12.8)	6.4 (23.7)	2.5 (9.2)	3.5 (13.0)	7.6 (28.1)	0.4 (1.3)	0.2 (0.8)	1.4 (5.1)
PEt ₂ Ph	36.2	1.0 (2.7)	3.5 (9.6)	6.0 (16.5)	2.9 (8.1)	—	9.0 (24.8)	5.0 (13.8)	7.1 (19.7)	1.8 (4.9)
PMe ₂ Ph	45.0	1.3 (2.3)	3.9 (8.6)	8.3 (18.4)	3.6 (7.9)	3.5 (7.8)	12.0 (26.6)	2.9 (6.4)	8.5 (18.8)	1.2 (2.6)
PEtPh ₂	87.1	1.5 (1.7)	15.0 (17.2)	24.0 (27.5)	11.4 (13.1)	11.4 (13.1)	7.9 (9.1)	1.5 (1.7)	13.4 (15.4)	1.0 (1.2)
PMePh ₂	95.4	1.3 (1.4)	14.9 (15.6)	29.0 (30.4)	13.9 (14.6)	3.8 (4.0)	16.0 (16.8)	0.9 (0.9)	12.1 (12.1)	3.4 (3.6)

a) NiCl₂(PR₃)₂ : 0.2 mmol; NaBH₄ : 2.0 mmol; isoprene : 4.8 ml; HMPA : 1.7 ml; reaction temperature : 80°C; reaction time : 13 h; numbers in parenthesis are selectivities.

the PPh₃ and PMePh₂ catalysts show the largest conversion when the ratio is 10, the activity order being PPh₃ ≈ PMePh₂ > PEtPh₂ >> PMe₂Ph > PEt₂Ph > PEt₃ ≈ PMe₃ (Table 2).

Some of oligomers could be rather selectively synthesized by proper choice of NaBH₄/Ni ratio and phosphorus ligand. For instance, the selectivity of 1,5,9-trimethyl-1,5,9-cyclododecatriene (TMCDT) is 40.9 and 35.1% with the PMe₃ and PMe₂Ph catalysts, respectively, at NaBH₄/Ni ratio of 3 and that of dimethylcyclooctadienes (DMCOD) is 37.4% with the PPh₃ catalyst.

The conversion after 18 h increases with the amount of NaBH₄, but levels off at the ratio of 12. The yields of dipentene (DP) and 2,6-dimethyl-1,3,6-octatriene (DMOT) increase, but those of other oligomers decrease on increasing the ratio. The yields of oligomers increase monotonically against the reaction time with all catalyst system, indicating their competitive formation.

Kinetics of oligomerization catalyzed by NiCl₂(PR₃)₂-NaBH₄ system. The logarithmic plots of reaction rates at the initial stage against the isoprene/Ni ratio, which was varied from 20 to 500, are shown in Fig. 1 to estimate the reaction order. The reaction order thus obtained strongly depends on the ligand and NaBH₄/Ni ratio. At a NaBH₄/Ni ratio of 3, the reaction orders of the PPh₃, PEtPh₂ and PEt₃ catalysts are -0.74, -0.27 and -0.05, respectively, however the reaction order of the PPh₃ catalyst increases to -0.28 at the NaBH₄/Ni ratio of 10. The reaction orders of zero or negative value suggest that the elimination step of the products from the catalyst is rate-determining, and that NaBH₄ as well as the phosphorus ligand influences this step. The addition of 1,5-cyclooctadiene or TMCDT to the PEtPh₂ catalyst system

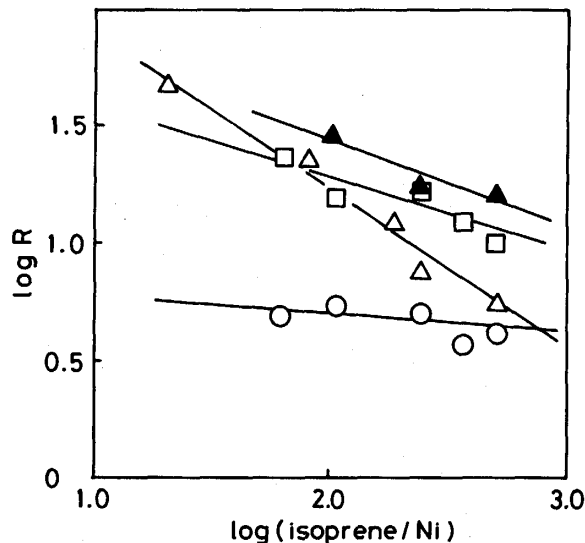


Fig. 1 Dependence of the reaction rate on the concentration of isoprene
 $\text{NiCl}_2(\text{PR}_3)_2$: 0.2mmol, reaction temperature: 80°C
 \triangle : PPh_3 , $\text{NaBH}_4/\text{Ni}=3$; \circ : PEt_3 , $\text{NaGH}_4/\text{Ni}=3$;
 \square : PEtPh_2 , $\text{NaBH}_4/\text{Ni}=3$; \blacktriangle : PPh_3 , $\text{NaBH}_4/\text{Ni}=10$

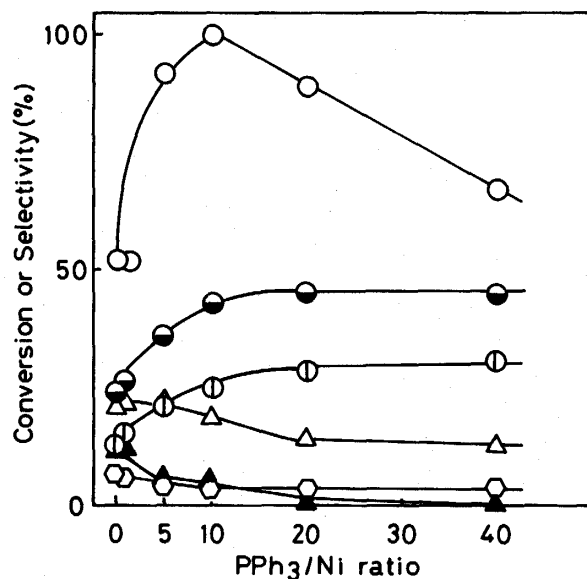


Fig. 2 Effects of the amount of PPh_3 on the rate of oligomerization
 $\text{NiCl}_2(\text{PPh}_3)_2$: 0.2mmol, isoprene: 4.8ml, NaBH_4 : 2mmol,
 HMPA: 1.7ml, reaction temperature: 80°C, reaction time: 7h
 \circ : conversion, \triangle : DMOT, \bullet : DP, \blacktriangle : TMDT, \circ : TMCDD

causes no change of the rate when the additive/Ni ratio is varied from zero to a hundred.

Effects of Excess Phosphorus Ligands on the Reaction Rate. The conversion and selectivity at a NaBH_4/Ni ratio of 10 are plotted against the amounts of excess PPh_3 added in Fig. 2, where the isoprene/Ni ratio is 240. The highest conversion is observed at PPh_3/Ni ratio of 10. Further excess PPh_3 decreases the conversion. The selectivities of DP and DMCOD increases with

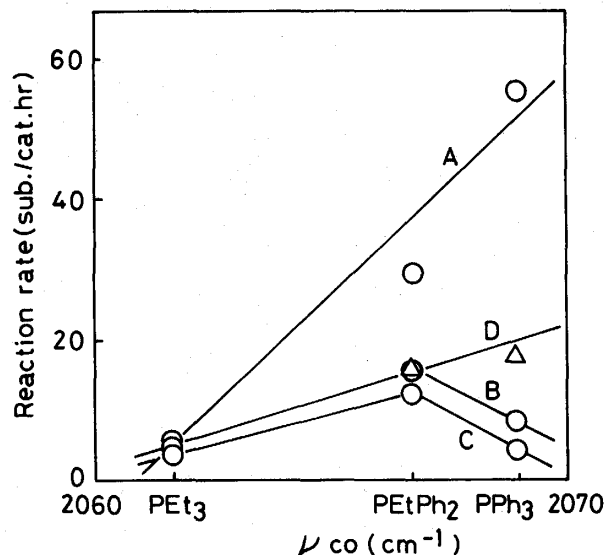


Fig. 3 Correlation between the catalytic activity of $\text{NiCl}_2(\text{PR}_3)_2$ and ν_{CO}
 $\text{NiCl}_2(\text{PR}_3)_2$: 0.2mmol, reaction temperature: 80°C,
 isoprene/Ni ratio: 20 (A), 240 (B, D), 500 (C)
 \circ : $\text{NaBH}_4/\text{Ni}=3$, \triangle : $\text{NaBH}_4/\text{Ni}=10$

excess PPh_3 , however, those of DMOT and trimers decrease. When NaBH_4/Ni ratio is 3, the increase of yields by the excess PPh_3 is more marked, however, the selectivities remain similar.

The conversion of isoprene and the yield of each oligomer in the presence of excess PPh_3 (PPh_3/Ni ratio of 100) increase linearly against the reaction time until the completion of the reaction, indicating the reaction order of zero, while it is -0.28 without excess PPh_3 .

Correlation of Kinetic Parameters with Electronic Characteristics of Ligands. The catalytic activities of nickel(0)-phosphorus complexes are correlated with values of carbonyl stretching frequency (ν_{CO}) of $\text{Ni}(\text{CO})_3\text{L}$ complexes⁵⁾ which are assumed to be the measures of electron donating abilities of the ligands (Fig. 3). The rate at $\text{NaBH}_4/\text{Ni}=3$ and isoprene/ $\text{Ni}=20$ increases linearly with ν_{CO} , whereas it varies in a volcano shape against ν_{CO} at higher isoprene/ Ni ratios (240 or 500). When NaBH_4/Ni ratio increases to 10, even at the higher concentrations of isoprene (for example: isoprene/ Ni ratio of 240) the reaction rate is proportionally correlated against ν_{CO} regardless of isoprene concentration. Variable reaction orders may account such correlation features. The low reaction order of the PPh_3 catalyst at the low NaBH_4/Ni ratio gives the small rate to the catalyst at the high isoprene concentration, resulting in a volcano shape correlation of the activity against ν_{CO} values. However, the higher NaBH_4/Ni ratio of 10 allows the higher reaction order (-0.28) for the PPh_3 catalyst, providing a linear correlation.

Correlations between the selectivity (described by yields ratios) and ν_{CO} are shown in Figs. 4 and 5, where NaBH_4/Ni ratios are 3 and 10, respectively. The $(\text{DP}+\text{trimers})/(\text{DMOD}+\text{DMOT})$

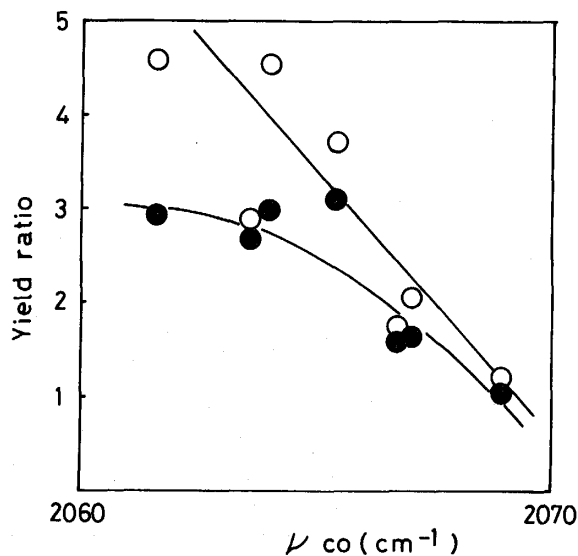


Fig. 4 Correlation between (trimer+DP)/(DMOD+DMCOD) ratio and ν co
 Reaction conditions: refer to Figs. 1 and 2.
 ○: $\text{NaBH}_4/\text{Ni}=3$, ●: $\text{NaBH}_4/\text{Ni}=10$

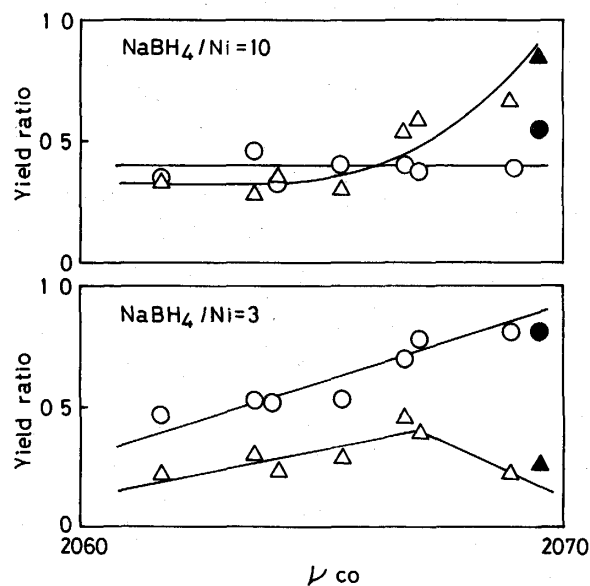


Fig. 5 Correlation between some selectivities and ν co.
 Reaction conditions: refer to Figs. 1 and 2
 ○: $\text{DMCOD}/(\text{DMCOD}+\text{DMOT}+\text{DMOD})$ ratio,
 △: $\text{DP}/(\text{DP}+\text{trimers})$ ratio,
 ●: $\text{DMCOD}/(\text{DMCOD}+\text{DMOT}+\text{DMOD})$ ratio, $\text{PPh}_3/\text{Ni}=10$,
 ▲: $\text{DP}/(\text{DP}+\text{trimers})$ ratio, $\text{PPh}_3/\text{Ni}=10$

+DMCOD) ratio linearly decreases against ν co at both ratios of NaBH_4/Ni , although some differences in the profiles are observable. At NaBH_4/Ni of 3, the $\text{DMCOD}/(\text{DMOD}+\text{DMOT}+\text{DMCOD})$ ratio linearly decreases against ν co and the $\text{DP}/(\text{trimer}+\text{DP})$ ratio increases against ν co from PEt_3 to PMePh_2 and suddenly decreases with the PPh_3 catalyst. At $\text{NaBH}_4/\text{Ni}=10$, the $\text{DMCOD}/(\text{DMOD}+\text{DMOT}+\text{DMCOD})$ ratio is constant regardless of ν co and the $\text{DP}/$

(trimers+DP) ratio linearly increases against ν co.

It should be noted that no relation between these kinetic parameters and cone angle of the ligand,⁵⁾ the steric factor, can be observed. The electronic factor may influence mainly the catalysis of the present systems.

Spectroscopic Study of Catalytic Species. The PPh_3 catalyst gives two broad peaks at 7.5 (free PPh_3) and -20ppm (coordinated PPh_3), in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum at 60°C , where the composition 0, in each components is the same as that under the reaction conditions. The amount of the free PPh_3 is estimated to be roughly 15%, rather independent of the NaBH_4/Ni ratio. Thus, considerable amounts of the ligand is liberated under the reaction conditions.

For the PEt_3 catalyst, two broad peaks of coordinated PEt_3 , which are located at -22 and -28ppm , respectively, are observed at all temperatures examined, excluding free PEt_3 ⁶⁾ ($19.0\sim 20.4\text{ppm}$) liberated from the catalyst during the catalytic reaction.

Mechanistic Consideration. A mechanism for the catalytic oligomerization has been proposed based on extensive studies. Although its essential framework may have been established,^{1,2)} some further details are necessary to understand or explain the product selectivity and catalytic activity including the reaction order or its total turnover number. In scheme 1, dimers are produced from intermediates either (I) or (II). Addition of one more isoprene molecule to (II) produces the intermediates (III) and (IV) which may lead trimers. The rate-determining step for the dimer production can be assumed to be the elimination of the products from the coordination sphere. In such a situation, nickel-carbon bond-strength influences the reaction rate of zero order kinetics, the weaker bond resulting in the faster reaction. The nickel-carbon bondstrength can be related to the value of co as postulated by Tolman.⁵⁾ Thus, the correlation between co values and the catalytic activities at the low concentration of isoprene (Fig. 3) can be deduced.

A negative reaction order observed with the PPh_3 catalyst causes the deviation from the correlation at the higher isoprene concentrations. The product inhibition, which often explains the negative order, is ruled out in the present case. The formation of catalytically inactive species due to high isoprene concentration may be the reason for the negative order. Although the phosphorus ligands can coordinate more strongly than isoprene and BH_4^- in the intermediate species such as (I) and (II), they can be replaced by isoprene when its concentration is high enough, leading to the inactive species. Thus, the reaction order may be lowered when the phosphorus ligand is more easily replaced by extra isoprene molecules. PPh_3 , the most labile ligand used, as revealed by ^{31}P -NMR in the present study, tends to allow the formation such inactive species under high isoprene concentrations, providing the lowest reaction order. The addition of excess NaBH_4 and/or PPh_3 can inhibit formation of inactive species by their coordination to the nickel ion, although excess phosphorus ligand may occupy all the coordination sites to form another inactive tris-tertiary phosphine species. In contrast, PEt_3 may hardly

allow the formation of the inactive intermediates because of its stable coordination. The strength of nickel-phosphorus ligand bond can be evaluated by the ν_{co} value, explaining the correlation.

The selectivities among the oligomeric products are assumed to be proportional to the concentration of intermediates (I), (II), (III) and (IV), according to the scheme. The (DP+trimers)/(DMOD+DMOT+DMCOD) ratio may correspond to that of intermediates II/I. A strongly electron-donating phosphine (described by ν_{co}) may stabilize the intermediate II (σ , π -allyl nickel) more preferably than the intermediate I (bis- π -allyl nickel),¹⁰⁾ producing more DP and trimers.

The DMCOD/(DMOD+DMOT+DMCOD) ratio may be related to the comparative reactivities of the intermediate I for the cyclization and the proton transfer of the substrate.^{4a)} A strongly electron-donating phosphorus ligand can be a better medium for the proton transfer, whereas a significant amount of NaBH_4 ($\text{NaBH}_4/\text{Ni}=10$) can be a proton source regardless of phosphorus ligands. The DP/(DP+trimers) ratio corresponds to the reactivity of the intermediate II. Another isoprene molecule may be easily inserted to the intermediate when some phosphorus ligands of weaker coordination abilities (smaller ν_{co} value) are liberated to open the site for it, producing more trimers. Thus, these selectivities are correlated to the value of ν_{co} .

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