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Fujitsu, Hiroshi
Institute of Advanced Material Study Kyushu University

Jono, Masahiro
Institute of Advanced Material Study Kyushu University

Okamoto, Hidenori
Institute of Advanced Material Study Kyushu University

Takeshita, Kenjiro
Institute of Advanced Material Study Kyushu University

他

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

Hiroshi FUJITSU, Masahiro JONO, Hidenori OKAMOTO,
Kenjiro TAKESHITA and Isao MOCHIDA

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 $Fe(acac)_3$-$AlEt_3$-Schiff-base catalyst.[3] The present authors have reported the enhanced activity of the $NiCl_2(PPh_3)_2$-$NaBH_4$ 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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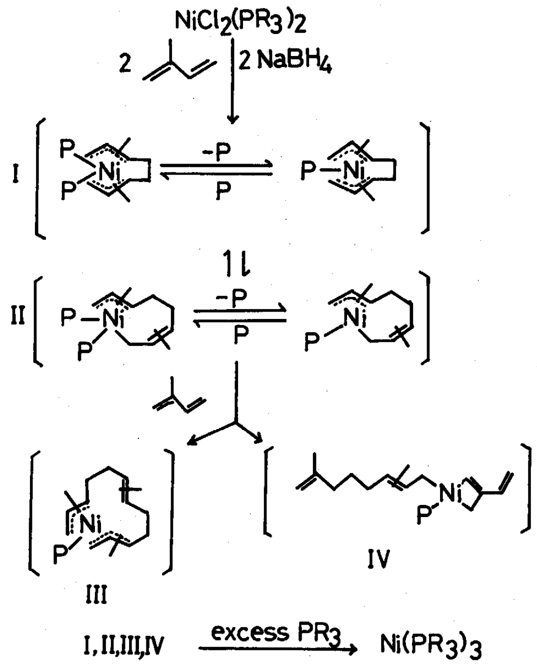
viewpoint in order the find ways to enhance the reaction rate to a practical level. The effects of type and amounts of phosphorus ligands in the catalytic system on the catalytic activity were emphasized, since Wilke et al.[2] reported that the activity was highest when one molecule of phosphorus ligand was coordinated to the catalyst complex. Tolman's conclusion on the electronic and steric characteristics of a series of ligands [5] may be another clue to the present approach. Some mechanistic details of the catalytic oligomerization could be discussed based on such results.

Experimental

$NiCl_2(PR_3)_2$(PR_3=PPh_3, ethyldiphenylphosphine ($PEtPh_2$), methyldiphenylphosphine (PMe Ph_2), diethylphenylphosphine (PEt_2Ph), dimethylphenylphosphine (PMe_2Ph), triethylphosphine (PEt_3), trimethylphosphine (PMe_3)) was prepared according to the method descrided 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.

Scheme



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-dimethy-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.

$^{31}P\{^1H\}$–NMR spectra were measured with an FT–NMR spectrometer (JEOL, JNE–FX100) at 40.32 NHz using 85% H_3PO_4 as an external reference. The samples of $NiCl_2(PR_3)_2$-$NaBH_4$ system were prepared from 0.5mmol $NiCl_2(PR_3)_2$, 1.5 or 5mmol $NaBH_4$, 10mmol (1ml) isoprene and 1.5ml (80mmol) dimethylacetamide. After 30 minutes' reaction at 80°C, $^{31}P\{^1H\}$–NMR spectra were measured at 60°C.

Results and Discussion

Catalytic Activities of $NiCl_2(PR_3)_2$-$NaBH_4$ System for the Oligomerization of Isoprene. Catalytic activities of $NiCl_2(PR_3)_2$-$NaBH_4$ with the system at an isoprene/Ni ratio of 240 ($NaBH_4$/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 $NaBH_4$. When the $NaBH_4$/Ni ratio is fixed at 3, the catalytic activity of the phoshorus complex catalysts decreases in the order $PMePH_2 \approx PEtPh_2 > PMe_2Ph > PPh_3 >> PMe_3 \approx PEt_2Ph > PEt_3$ (Table 1). In contrast,

Table 1. Effects of phosphorus ligands on the oligomerization of isoprene.[a]

		Yield (%)								
Ligand	Conv (%)	DMOD	DMOT	DP	DMCOD	TMDT	TMCDT	Other trimers	Tetra-mers	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_2Ph	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_2Ph	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] $NiCl_2(PR_3)_2$: 0.2 mmol; $NaBH_4$: 0.6 mmol; isoprene : 4.8 ml; HMPA : 1.7 ml; reaction temperature : 80℃; reaction time : 24 h; numbers in parenthesis are selectivities.

Table 2. 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	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_2Ph	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_2Ph	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) $NiCl_2(PR_3)_2$: 0.2 mmol; $NaBH_4$: 2.0 mmol; isoprene : 4.8 ml; HMPA : 1.7 ml; reaction temperature : 80℃; reaction time : 13 h; numbers in parenthesis are selectivities.

the PPh_3 and $PMePh_2$ catalysts show the largest conversion when the ratio is 10, the activity order being $PPh_3 \approx PMePh_2 > PEtPh_2 >> PMe_2Ph > PEt_2Ph > PEt_3 \approx PMe_3$ (Table 2).

Some of oligomers could be rather selectively synthesized by proper choice of $NaBH_4$/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 PMe_3 and PMe_2Ph catalysts, respectively, at $NaBH_4$/Ni ratio of 3 and that of dimethylcycloctadienes (DMCOD) is 37.4% with the PPh_3 catalyst.

The conversion after 18 h increases with the amount of $NaBH_4$, 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 $NiCl_2(PR_3)_2$-$NaBH_4$ 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 $NaBH_4$/Ni ratio. At a $NaBH_4$/Ni ratio of 3, the reaction orders of the PPh_3, $PEtPh_2$ and PEt_3 catalysts are −0.74, −0.27 and −0.05, respectively, however the reaction order of the PPh_3 catalyst increases to −0.28 at the $NaBH_4$/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 $NaBH_4$ as well as the phosphorus ligand influences this step. The addition of 1,5-cyclooctadiene or TMCDT to the $PEtPh_2$ catalyst system

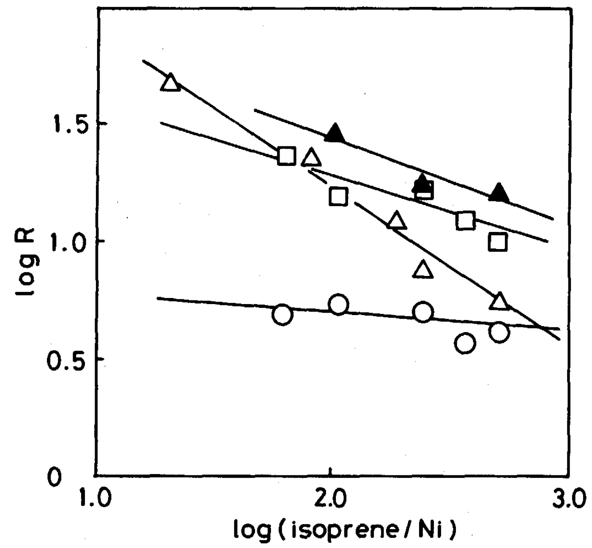


Fig. 1 Dependence of the reaction rate on the concentration of isoprene
$NiCl_2(PR_3)_2$: 0.2mmol, reaction temperature: 80°C
△: PPh_3, $NaBH_4/Ni=3$; ○: PEt_3, $NaGH_4/Ni=3$;
□: $PEtPh_2$, $NaBH_4/Ni=3$; ▲: PPh_3, $NaBH_4/Ni=10$

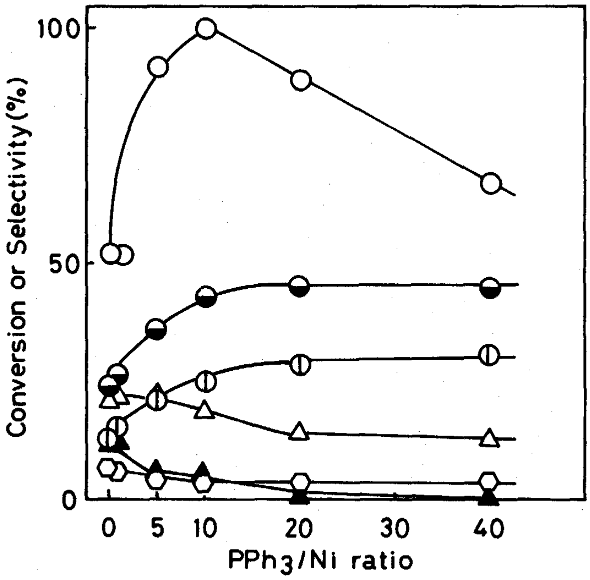


Fig. 2 Effects of the amount of PPh_3 on the rate of oligomerization
$NiCl_2(PPh_3)_2$: 0.2mmol, isoprene: 4.8ml, $NaBH_4$: 2mmol,
HMPA: 1.7ml, reaction temperture: 80°C, reaction time: 7h
○: conversion, △: DMOT, ◒: DP, ▲: TMDT, ⬡:TMCDT

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. Te 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

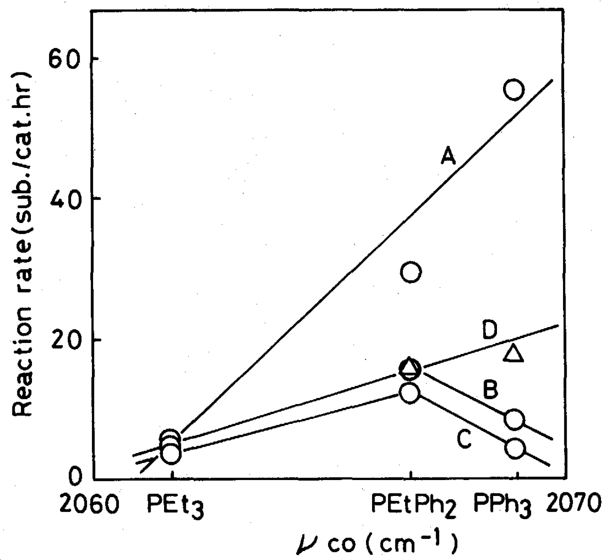


Fig. 3 Correlation between the catalytic activity of $NiCl_2(PR_3)_2$ and ν co
$NiCl_2(PR_3)_2$: 0.2mmol, reaction temperature: 80°C,
isoprene/Ni ratio: 20 (A), 240 (B, D), 500 (C)
○: $NaBH_4/Ni=3$, △: $NaBH_4/Ni=10$

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 $Ni(CO)_3L$ complexes[5] which are assumed to be the measures of electron donating abilities of the ligands (Fig. 3). The rate at $MaBH_4/Ni=3$ and isoprene/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 (DP+trimers)/(DMOD+DMOT

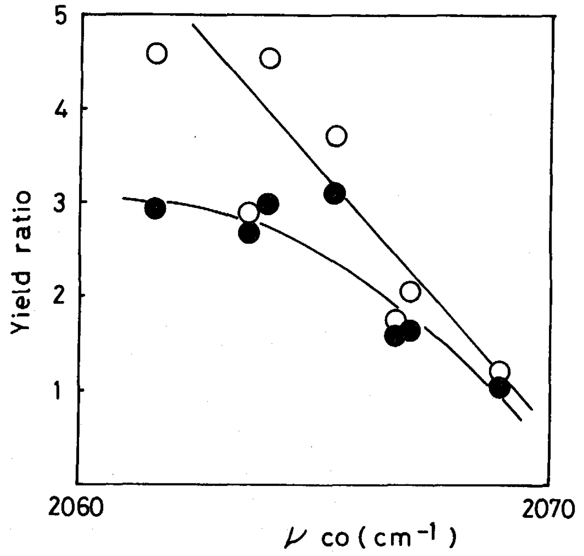


Fig. 4 Correlation between (trimers+DP)/(DMOD+DMCOD) ratio and ν co
Reaction conditions: refer to Figs. 1 and 2.
○: $NaBH_4/Ni=3$, ●: $NaBH_4/Ni=10$

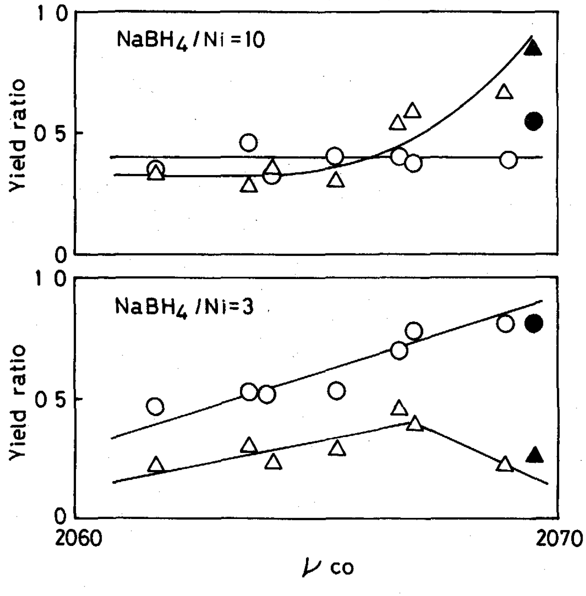


Fig. 5 Correlation between some selectivities and ν co.
Reaction conditions: refer to Figs. 1 and 2
○: DMCOD/(DMCOD+DMOT+DMOD) ratio,
△: DP/(DP+trimers) ratio,
●: DMCOD/(DMCOD+DMOT+DMOD) ratio, $PPh_3/Ni=10$,
▲ : DP/(DP+trimers) ratio, $PPh_3/Ni=10$

+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 DMCOD/(DMOD+DMOT+DMCOD) ratio linearly decreases against ν co and the DP/(trimers+DP) ratio increases against ν co from PEt_3 to $PMePh_2$ and suddenly decreases with the PPh_3 catalyst. At $NaBH_4/Ni=10$, the DMCOD/(DMOD+DMOT+DMCOD) ratio is constant regardless of ν co and the 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}P{^{1}H}−NMR specrum 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] (19.0～20.4ppm) 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 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 coorelation 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 higt 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 reavealed 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), accrding 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 con be a better medium for the proton transfer, whereas a significant amount of $NaBH_4$($NaBH_4$/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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References

1) (a) P.W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Academic Press, New York and London, 1974.
   (b) P. Heimbach, P. W. Jolly and G. Wilke, Adv. Organometal. Chem., **8,** 29 (1970).
2) W. Brenner, P. Heimbach, H. Hey, E.W. Muller, and G. Wilke, Angew. Chem., **727,** 161 (1969).
3) W. Ching-Yong and E. Swift, J. Catal., **24,** 510 (1971).
4) (a) I. Mochida, S. Yuasa, and T. Seiyama, J. Catal., **41,** 101 (1976).
   (b) I. Mochida, K. Kitagawa, H. Fujitsu, and K. Takeshita, J. Catal., **54,** 175 (1978).
   (c) I. Mochida, H. Okamoto, K. Kitagawa, H. Fujistu, and K. Takeshita, Ind. Eng. Chem. Prod. Res. Dev., **19,** 392 (1980).
5) C. A. Tolman, Chem. Revs., **77,** 313 (1977).
6) H. Itatani and J. C. Bailar, Jr., J. Am. Chem. Soc., **89,** 1500 (1967).
7) M. A. Beg and C. Clark, Canad. J. Chem., **39,** 595 (1961).
8) R. C. cass, G. E. Coates, and R. G. Hayter, J. Chem. Soc., **1955,** 4007.
9) G. E. Coates and C. Parkin, J. Chem. Sco., **1963,** 421.
10) G. H. Olive and S. Olive, Angew. Chem. Internat. Ed., **19,** 105 (1971).