

EFFECTS OF DITERTIARY PHOSPHINE LIGANDS IN COOLIGOMERIZATION OF  
ETHYLENE AND BUTADIENE BY NICKEL BASED CATALYST

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In the reactions of ethylene and butadiene catalyzed by  $\text{CoCl}_2$ - $\text{AlEt}_3$ -phosphine system(1) and by  $\text{FeCl}_3$ - $\text{AlEt}_3$ -phosphine system(2), it has been reported that the bidentate ditertiary phosphine ligand, especially 1,2-bis(diphenylphosphino)ethane gives 1,4-hexadiene with high selectivity. We have found that in the cooligomerization of ethylene and butadiene by  $\text{NiCl}_2$ - $\text{AlEt}_3$ -ditertiary phosphine catalyst system, the structure and concentration of ditertiary phosphine control the reaction products drastically. Moreover, we have found the high selective catalysts for the formation of 1,4,9-decatriene. To our knowledge, such high selective catalysts have not been reported.

When the reaction of ethylene and butadiene was catalyzed by  $\text{NiCl}_2$ - $\text{AlEt}_3$ -1,2-bis(diphenylphosphino)ethane (DPE) in toluene solvent at  $110^\circ$  under ethylene pressure of  $50 \text{ kg/cm}^2$  for 3 hr without air, the cooligomerization product was 1,4,9-decatriene where the mole ratio of DPE to  $\text{NiCl}_2$  was less than unity. When the mole ratio of DPE to  $\text{NiCl}_2$  was more than unity in the above reaction, 1,4-hexadiene produced exclusively as the only cooligomerization product. However, when the mole ratio of DPE to  $\text{NiCl}_2$  reached 3, the reaction stopped almost completely at  $110^\circ$ . 1,3-Bis(diphenylphosphino)propane (DPP) ligand shows the trend similar to DPE, i.e.

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in the case of DPP mole/ $\text{NiCl}_2$  mole  $< 1$ , the cooligomerization product was 1,4,9-decatriene, while in the case of DPP mole/ $\text{NiCl}_2$  mole = 1.5, the sole cooligomerization product was 1,4-hexadiene. It is rare that the concentration of the ligand in the catalyst system discriminates the reaction products such drastically as these cases. The product 1,4,9-decatriene was identified by n.m.r. ( $\tau$  3.7 - 4.5 (2H), 4.5 - 4.6 (2H), 4.7 - 5.2 (4H), 7.1 - 7.5 (2H), 7.6 - 8.2 (4H), 8.3 - 8.9 (2H)), I.R. and the chemical reactions, i.e. it absorbed 3 moles of hydrogen in the presence of Pd-C catalyst in methanol to convert into n-decane and absorbed 3 moles of bromine in acetic acid at room temperature. Bis(diphenylphosphino)methane (DPM) ligand shows somewhat different behaviors. In the case of DPM mole/ $\text{NiCl}_2$  mole  $\leq 2$ , the main cooligomerization product was 1,4,9-decatriene with some 1,4,8-decatriene. In the case of DPM/ $\text{NiCl}_2 = 3$ , the reaction stopped completely at  $110^\circ$ . However, in the case of  $3 > \text{DPM}/\text{NiCl}_2 > 2$ , the product was also 1,4,9-decatriene though a smaller yield, and no 1,4-hexadiene produced. Triphenylphosphine ligand does not show at all the selectivity for the cooligomerization of ethylene and butadiene. It formed many products including butadiene oligomers. Some experimental results are shown in Table 1.

Table 2. The Effect of  $\text{NiCl}_2 \cdot n\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  for Formation of 1,4,9-Decatriene<sup>a)</sup>

Ligand	Butadiene	Total yield of products	1,4,9-DT <sup>b)</sup>
n	(g)	(g)	(g)
1	31	17	14
2	32	c)	0
3	33	9.5	7.4
4	33	23	14
5	33	26	10
6	34	28	7.1
10	32	25	6.3

a) See footnote (a) of Table 1

b) 1,4,9-DT = 1,4,9-decatriene

c) Specific reaction. See the text.

Table 1. The Effect of Mole Ratio of 1,2-Bis(diphenylphosphino)ethane to  $\text{NiCl}_2$  for the Ethylene-Butadiene Oligomerization<sup>a)</sup>

DPE/Ni (mole/ mole)	BD(g) <sup>b)</sup>	Total Yield of Products (g)	Product (g)					Higher oligomer of BD
			HD <sup>c)</sup>	VCH <sup>d)</sup>	COD <sup>e)</sup>	DT <sup>f)</sup>	CDT <sup>g)</sup>	
0	33	27	t	1.5	1.5	7	4.8	+
0.5	34	35	t	2.0	1.5	18	6.0	+
1.0	30	27	t	1.5	2.0	14	6.3	+
1.05	31	25	22	t	-	t	-	
1.25	32	26	23	t	-	t	-	
1.5	33	28	27	t	-	-	-	
2.0	32	26	25	t	-	-	-	
2.5	34	19	17	t	-	t	-	
3.0	32	1	1	-	-	-	-	

a)  $\text{NiCl}_2 = 6.02 \times 10^{-4}$  moles,  $\text{AlEt}_3 = 1.14 \times 10^{-2}$  moles,  
toluene 5ml,  $110^\circ\text{C}$ , 3 hr,  
ethylene pressure =  $50 \text{ kg/cm}^2$ .

b) BD = butadiene,

c) HD = 1,4-hexadiene

d) VCH = vinylcyclohexene,

e) COD = cyclooctadiene,

f) DT = 1,4,9-decatriene,

g) CDT = cyclododecatriene

The effects of n of the previously prepared  $\text{NiCl}_2$ -ditertiary phosphine complexes  $\text{NiCl}_2 \cdot \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  for the 1,4,9-decatriene formation are shown in Table 2. Where n=1 or 3, the proportion of 1,4,9-decatriene in the products was remarkably high. In the case of n=6 or 10, the ligand effects for the selectivity of 1,4,9-decatriene did not appear and the product distribution was similar to the  $\text{NiCl}_2$ - $\text{AlEt}_3$  catalyst. It is very interesting that the highly pure  $\text{NiCl}_2 \cdot \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  complex was almost completely inert to the above reaction at  $110^\circ$ . In this case, both oligomerization and cooligomerization did not occur, but the brown "liquid complex" produced which was air sensitive and contained nickel. When small amounts of  $\text{NiCl}_2$

were added to the "liquid complex", the resulting mixture became a highly selective catalyst for 1,4,9-decatriene formation. The structure and chemical behaviors of this "liquid complex" are in progress.

## REFERENCES

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