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# Ligand Effects in the Cooligomerization of Butadiene and Ethylene by a Nickel-based Catalyst System[1]

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The cooligomerization of butadiene and ethylene catalyzed by a $NiCl_2$–$AlEt_3$–phosphine system was investigated. The cooligomerization product was 1,*cis*-4-hexadiene or/and 1,*trans*-4,9-decatriene. Bidentate ditertiary phosphines had remarkable effects on the reaction. The effects of ditertiary phosphines are also described.

Several complex catalyst systems for the cooligomerization of a conjugated diene and a monoolefin have been reported. Iwamoto reported the codimerization of butadiene and ethylene to give 1,*cis*-4-hexadiene by means of a catalyst system composed of cobalt chloride, ditertiary phosphine, and triethylaluminum.[2] An iron-based catalyst system for the synthesis of 1,*cis*-hexadiene has also been reported.[3] Müller and his coworkers found the reaction of butadiene and ethylene to give 1,5,9-decatriene.[4] Wilke reported a cotrimerization of butadiene and ethylene giving *trans*-1,*cis*-5-cyclodecadiene and 1,*trans*-4,9-decatriene by means of a nickel acetylacetonate-diethylaluminum ethoxide catalyst system.[5] The addition of α-olefins to conjugated dienes was accomplished by means of a catalyst derived from the interaction of bis(tri-*n*-butylphosphine) nickel chloride, and diisobutylaluminum chloride.[6] Linear 1,4-dienes were the primary products. The synthesis of 1,*trans*-4-hexadiene with rhodium trichloride was reported by Alderson.[7] A detailed study of the reaction of butadiene and ethylene catalyzed by a nickel hydride complex, $HNi(P(OEt)_3)_4^+$, was also reported.[8]

In a previous paper, the present authors reported briefly on the cooligomerization of butadiene and ethylene by means of a nickel-based catalyst system;[9] in this paper, they will describe the effects of ditertiary phosphine in the catalyst system.

## Experimental

*Reagents.* The toluene was purified by washing it with sulfuric acid and by then distilling it over sodium under a nitrogen atmosphere. The triethylaluminum and ethylene were used without further purification. The butadiene was dried by passing it through columns of calcium chloride and of silica gel. The nickel chloride and triphenylphosphine were commercial reagents. The ditertiary phosphines were prepared according to the method described by Hewertson and Watson.[10] Nickel complexes of the phosphines were prepared by adding nickel chloride to an alcoholic solution of the phosphines.

| Ditertiary phosphine | Mp (°C) |
|---|---|
| $Ph_2P(CH_2)_nPPh_2$ | |
| $n=1$ | 119.9—120.9(120.5—121.5)[10] |
| $n=2$ | 139.6—140.9(143—144)[10] |
| $n=3$ | 63.3—65.3(61—62)[2,11] |
| $n=4$ | 133.8—133.9(137—139)[12] |
| $n=5$ | 43.1—46.1(liquid)[12] |
| $n=6$ | 125.2—126.0 |
| $Ph_2PCH_2OCH_2PPh_2$ | 90.3—95.3 |
| $Ph_2PCH_2CH_2OCH_2CH_2PPh_2$ | liquid (liquid)[12] |

*Procedure.* A 100 m*l* stainless-steel autoclave equipped with a magnetic stirrer was charged with nickel chloride, ditertiary phosphine (or its nickel complex), toluene (with or without), butadiene, and triethylaluminum in a glass ampoule under a nitrogen atmosphere. At room temperature, ethylene was introduced until a pressure of *ca.* 20 kg/cm$^2$ was reached, after which the ampoule of triethylaluminum was broken with agitation. Then the autoclave was heated to 110°C, where the reaction pressure reached approximately 50 kg/cm$^2$; this pressure was maintained during the reaction by introducing ethylene. After 3 hr, the autoclave was cooled to room temperature and the catalyst was quenched by adding a small amount of methanol. The reaction mixture was washed with water and dried with anhydrous sodium sulfate. The products were analyzed by gas chromatography.

*Product Analysis.* *1,* trans*-4, 9-Decatriene*: 1, *trans*-4, 9-Decatriene was distilled from the reaction mixture at 83°C/52 mmHg. The IR spectrum of the compound exhibited absorption bands at 3065, 1637, 987, 965, and 910 cm$^{-1}$, showing the existence of terminal vinyl and *trans* double-bond groups. No peak attributable to conjugated diene was observed. NMR spectrum showed a very complicated pattern. The signals at $\tau=3.7$—4.6(4H), 4.7—5.2(4H), 7.1—7.5(2H), 7.6—8.2(4H), and 8.3—8.9(2H) were attributable to $-C=CH-$, $-C=CH_2$, $=C-CH_2-C=$, $-C-CH_2-C=$, and $-C-CH_2-C-$ respectively. Hydrogenation was carried out in methanol at 50°C by means of a palladium black catalyst under an atmospheric hydrogen pressure. Three moles of hydrogen were absorbed, and *n*-decane was obtained.

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[1] Ligand effects. II.

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[9] Y. Inoue, T. Hagawa, and H. Hashimoto, *Tetrahedron Lett.*, **1970**, 1099.

[10] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.

[11] G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1960 (1966).

[12] L. Sacconi and J. Gelsomini, *Inorg. Chem.*, **7**, 291 (1968).

The gas chromatogram of the reaction mixture showed a shoulder peak on that of 1,4,9-decatriene, the fraction of which was separated by preparative gas chromatography. The IR spectrum of the compound exhibited a pattern fairly similar to that of 1,4,9-decatriene. The peaks at 3075, 1634, 1374, 989, 965, and 912 cm$^{-1}$ showed the existence of terminal vinyl, *trans* double-bond, and methyl groups. No peak attributable to conjugated diene was observed. The peaks at 989 and 912 cm$^{-1}$, attributable to the terminal vinyl group, were weaker than those of 1,4,9-decatriene. On the hydrogenation of a mixture of the compound and 1,4,9-decatriene, only *n*-decane was formed. The compound is presumed to be 1,4,8-decatriene.

*1,*cis*-4-Hexadiene*: 1,*cis*-4-Hexadiene was distilled from a reaction mixture at 66.5—67.0°C. Its IR and NMR spectra were identical with those of an authentic sample of the *cis* isomer.

4-Vinylcyclohexene, 1,5-cyclooctadiene, and 1,5,9-cyclododecatriene were identified by gas chromatography, and by IR and NMR spectroscopy.

## Results and Discussion

*1. $NiCl_2$–$AlEt_3$ System.* In the reaction of butadiene and ethylene with this catalyst system, the main products were higher oligomers. 4-Vinylcyclohexene(VCH), 1,5-cyclooctadiene(COD), 1,4,9-decatriene(DT), and 1,5,9-cyclododecatriene(CDT) were also produced. The selectivity of the DT(DT(g)/products (g)) was about 25 wt%. The yield of 1,4-hexadiene (HD) was negligible.

*2. $PPh_3$–$NiCl_2$–$AlEt_3$ System.* In this catalyst system, the main products were also higher oligomers. The increase in triphenylphosphine suppressed the formation of DT and CDT.

*3. $Ph_2PCH_2PPh_2$(DPM)–$NiCl_2$–$AlEt_3$ System.* The main cooligomerization product was 1,4,9-decatriene, plus some 1,4,8-decatriene. The yield of 1,4-hexadiene was also negligible.

When the molar ratio of DPM to $NiCl_2$ reached 3, the reaction stopped almost completely.

Table 1. Effects of $PPh_3$
$NiCl_2=6.02\times10^{-4}$ mol, 110°C, 3 hr, 50 kg/cm, toluene 5 m*l* as solvent

| $PPh_3$/Ni (mol/mol) | Al/Ni (mol/mol) | BD[a] (g) | Yield (g) | Products (wt%) VCH | COD | DT | CDT |
|---|---|---|---|---|---|---|---|
| 0 | 19 | 33 | 27 | 3.7 | 4.3 | 26 | 18 |
| 2[b] | 18 | 25 | 21.5 | 1.4 | 4.7 | 23 | 4.7 |
| 5 | 18 | 33 | 22.2 | 1.4 | 15 | 17 | trace |

a) BD=butadiene
b) $Ni(PPh_3)_2Cl_2$ complex $5.61\times10^{-4}$ mol

Table 2. Effects of DPM
$NiCl_2=6.02\times10^{-4}$ mol, 110°C, 3 hr, 50 kg/cm$^2$ toluene 5 m*l* as solvent

| DPM/Ni (mol/mol) | Al/Ni (mol/mol) | BD (g) | Yield (g) | Products (wt%) VCH | COD | DT[b] | CDT |
|---|---|---|---|---|---|---|---|
| 0 | 19 | 33 | 27 | 3.7 | 4.3 | 26 | 18 |
| 1 | 19 | 32 | 29 | 7.9 | 8.6 | 38 | 13 |
| 2 | 18 | 33 | 28 | 9.4 | 10 | 33 | 5.5 |
| 2[a] | 25 | 31 | 17 | 5.9 | 5.9 | 70 | 7.6 |
| 2.25 | 19 | 31 | 6.5 | 23 | 12 | 46 | 15 |
| 3 | 18 | 40 | 1.0 | + | + | + | + |

a) $Ni(DPM)_2Cl_2$ complex $4.55\times10^{-4}$ mol
b) DT=1,4,9-+1,4,8-decatriene

*4. $Ph_2PCH_2CH_2PPh_2$(DPE)–$NiCl_2$–$AlEt_3$ System.* The main cooligomerization product was 1,4,9-decatriene when the molar ratio of DPE to $NiCl_2$ was less than unity. However, when the ratio exceeded unity, the sole cooligomerization product was 1,4-hexadiene. When the molar ratio of DPE to $NiCl_2$ reached 3, the reaction stopped almost completely at 110°C. If the reaction temperature was elevated to 130°C, the catalytic activity was observed even though the molar ratio of DPE to $NiCl_2$ was 4.

Table 3. Effects of DPE
$NiCl_2=6.02\times10^{-4}$ mol, $AlEt_3=1.14\times10^{-2}$ mol, 110°C, 3 hr, 50 kg/cm$^2$, toluene 5 m*l* as solvent

| DPE/Ni (mol/mol) | BD (g) | Yield (g) | Products (wt%) HD[a] | VCH | COD | DT | CDT | Higher oligomers |
|---|---|---|---|---|---|---|---|---|
| 0 | 33 | 27 | trace | 3.7 | 4.3 | 26 | 18 | + |
| 0.5 | 34 | 35 | trace | 4.3 | 4.0 | 51 | 17 | + |
| 1.0 | 30 | 27 | trace | 5.5 | 10 | 54 | 23 | + |
| 1.05 | 31 | 25 | 87 | trace | — | trace | — | — |
| 1.25 | 32 | 26 | 88 | trace | — | trace | — | — |
| 1.5 | 33 | 28 | 96 | trace | — | — | — | — |
| 2.0 | 32 | 26 | 95 | trace | — | — | — | — |
| 2.5 | 34 | 19 | 89 | trace | — | trace | — | — |
| 3.0 | 32 | 1 | + | + | — | — | — | — |
| 4.0[b] | 25 | 20 | 95 | trace | — | — | — | — |

a) HD=1,4-hexadiene b) 130°C, 1 hr

It was expected that triethylaluminum took an important role in the cooligomerization reaction of butadiene and ethylene. To ascertain the effect of triethylaluminum, the molar ratio of triethylaluminum to nickel chloride was gradually changed at $DPE/NiCl_2=0.5$ and the distribution of the products was examined.

Table 4. Effects of $AlEt_3$
$NiCl_2=6.02\times10^{-4}$ mol, DPE/Ni=0.5, 110°C, 3 hr, 50 kg/cm$^2$

| Al/Ni (mol/mol) | BD (g) | Yield (g) | Products (wt%) HD | VCH | COD | DT | CDT | Higher oligomers |
|---|---|---|---|---|---|---|---|---|
| 3.1 | 28 | 24 | 41 | 2.6 | 4.6 | 18 | 8.4 | + |
| 4.2 | 25 | 19 | 24 | 2.9 | 5.8 | 27 | 8.3 | + |
| 8.3 | 27 | 27 | 0.4 | 3.1 | 4.2 | 27 | 9.3 | + |
| 19.6 | 34 | 35 | trace | 4.4 | 4.0 | 51 | 17 | + |

When the molar ratio of triethylaluminum to nickel chloride was 19.5, 1,4-hexadiene was not produced; 1,4,9-decatriene was obtained as the main cooligomerization product. However, the molar ratio of triethyl aluminum to nickel chloride became 3.1, 1,4-hexadiene and 1,4,9-decatriene were obtained together. There was a tendency for the yield of 1,4-hexadiene to increase as the molar ratio of triethylaluminum to nickel chloride became smaller.

As was suggested in discussing the reaction of butadiene with ethylene catalyzed by the $HCo(Ph_2PCH_2CH_2PPh_2)_2$–triethylaluminum system,[13] it seems that triethylaluminum can interact with the coordinated phosphorus atom, release it from the metal atom, and make a coordinatively unsaturated state. This interaction should be more effective at a higher concentration of triethylaluminum. The coordinatively unsaturated state would promote the reaction of butadiene with ethylene. It would depend on the degree of unsaturation whether 1,4,9-decatriene or 1,4-hexadiene was produced. Clearly, the formation of 1,4,9-decatriene requires a higher unsaturated state around the nickel atom than that of 1,4-hexadiene, and so it is always accompanied by other products, such as VCH, COD, and CDT.

It is very interesting to note that the $Ni(DPE)Cl_2$–$AlEt_3$ system showed no catalytic activity for the cooligomerization of butadiene and ethylene. However, the addition of $NiCl_2$ to the catalyst system caused the catalytic activity for the butadiene-ethylene reaction to recover and 1,4,9-decatriene was yielded. A Lewis acid such as $AlCl_3$ or $FeCl_3$ was ineffective, unlike $NiCl_2$. On the other hand, the addition of DEP to the $Ni(DPE)Cl_2$–$AlEt_3$ system did not cause any catalytic activity. The effect of the added $NiCl_2$ is shown in Table 5.

TABLE 5. EFFECTS OF $NiCl_2$ ADDED TO $Ni(DPE)Cl_2$–$AlEt_3$ SYSTEM
$Ni(DPE)Cl_2 = 5.68 \times 10^{-4}$ mol,
$Al/Ni(DPE)Cl_2 = 18.5$—$20.2$,
110°C, 3 hr, 50 kg/cm$^2$

| $NiCl_2/Ni(DPE)Cl_2$ (mol/mol) | BD (g) | Yield (g) | DT (g) |
|---|---|---|---|
| 3.1 | 36 | 0.5 | trace |
| 6.8 | 32 | 9.0 | 5.1 |
| 13.5 | 40 | 27.0 | 12.0 |
| 27.0 | 34 | 27.5 | 15.0 |

5. *$Ph_2P(CH_2)_3PPh_2$(DPP)–$NiCl_2$–$AlEt_3$ System.* The DPP ligand showed almost the same catalytic effect as DPE; *i.e.*, when the molar ratio of DPP to $NiCl_2$ was less than unity, the main cooligomerization product was 1,4,9-decatriene and 1,4-hexadiene was produced. When it was more than unity, 1,4,9-decatriene was not produced and 1,4-hexadiene was the sole cooligomerization product. In contrast with the catalyst system containing DPE, the reaction did not stop even at $DPP/NiCl_2 = 5$ at 110°C.

TABLE 7. EFFECTS OF DPB
$NiCl_2 = 6.02 \times 10^{-4}$ mol, 110°C, 3 hr, 50 kg/cm$^2$

| DPB/Ni (mol/mol) | Al/Ni (mol/mol) | BD (g) | Yield (g) | Products (wt%) VCH | COD | DT | CDT | Higher oligomers |
|---|---|---|---|---|---|---|---|---|
| 0 | 19 | 33 | 27 | 3.7 | 4.3 | 26 | 18 | + |
| 1.0[a)] | 22 | 33 | 23 | + | + | 62 | + | + |
| 1.5 | 19 | 33 | 11 | 29 | 15 | 16 | 7.2 | + |
| 2.0 | 18 | 37 | 11 | 25 | 9.4 | 5.7 | 3.8 | + |

a) $Ni(DPB)Cl_2$ complex $5.58 \times 10^{-4}$ mol

6. *$Ph_2P(CH_2)_4PPh_2$(DPB)–$NiCl_2$–$AlEt_3$ System.* In this reaction system, the main products were higher oligomers, and no formation of 1,4-hexadiene was observed.

7. *Other Bidentate Ligands–$NiCl_2$–$AlEt_3$ Systems.* In the reaction of the complexes coordinated with $Ph_2P(CH_2)_nPPh_2$ ($n$=5,6), $Ph_2PCH_2OCH_2PPh_2$, and $Ph_2PCH_2CH_2OCH_2CH_2PPh_2$, no ligand effects were observed distinctly. The distribution of products resembled that of the $NiCl_2$–$AlEt_3$ system.

In the present study, the added or coordinated ditertiary phosphine had a great influence on the distribution of products. When the molar ratio of DPE or DPP to $NiCl_2$ became unity, a great change in the distribution of products was observed.

TABLE 8. EFFECTS OF THE OTHER BIDENTATE LIGANDS
110°C, 3 hr, 50 kg/cm$^2$, toluene 5 m*l* as solvent

| Complex (g) | Al/Ni (mol/mol) | BD (g) | Yield (g) | DT (g) |
|---|---|---|---|---|
| $Ni(DPPE)Cl_2$ 0.310 | 23 | 33 | 26 | 10 |
| $Ni(DPH)Cl_2$ 0.320 | 18 | 34 | 28 | 7.1 |
| $Ni(DPMO)Cl_2$ 0.315 | 22 | 33 | 29 | 9.6 |
| $Ni(DPEO)Cl_2$ 0.310 | 25 | 39 | 37 | 20 |

$DPPE = Ph_2P(CH_2)_5PPh_2$, $DPH = Ph_2P(CH_2)_6PPh_2$,
$DPMO = Ph_2PCH_2OCH_2PPh_2$,
$DPEO = Ph_2PCH_2CH_2OCH_2CH_2PPh_2$

TABLE 6. EFFECTS OF DPP
$NiCl_2 = 6.02 \times 10^{-1}$ mol, 110°C, 3 hr, 50 kg/cm$^2$

| DPP/Ni (mol/mol) | Al/Ni (mol/mol) | BD (g) | Yield (g) | Products (wt%) HD | VCH | COD | DT | CDT | Higher oligomers |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 19 | 33 | 27 | trace | 3.7 | 4.3 | 26 | 18 | + |
| 0.5 | 17 | 29 | 26 | trace | 5.9 | 10.8 | 37 | 20 | + |
| 1.0[a)] | 20 | 33 | 9.5 | trace | + | + | 73 | + | + |
| 1.5 | 17 | 33 | 15 | 96 | trace | — | — | — | — |
| 3.0 | 17 | 31 | 27 | 97 | trace | — | trace | — | — |
| 5.0 | 18 | 29 | 29 | 98 | trace | — | — | — | — |

a) $Ni(DPP)Cl_2$ complex $5.62 \times 10^{-4}$ mol

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[13] M. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **71**, 237 (1968).

Generally, a phosphine ligand coordinates to a low-valent nickel atom which is produced by reduction with an organoaluminum compound, and stabilizes it. This function of a phosphorus atom is stronger with bidentate ditertiary phosphine than with monodentate phosphine because of its chelating effect. Especially, the chelation of the ditertiary phosphines, $Ph_2P(CH_2)_nPPh_2$ ($n=2,3$), is stronger than those of the other ditertiary phosphines because of the easy formation of a five- or six-membered chelate ring. The high coordinating ability of DPE and DPP is supposed to be the promoting power for the selective formation of 1,4-hexadiene.