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Effects of Ditertiary Phosphine Ligands in Co-dimerization of Butadiene and Ethylene Catalyzed by Cobaltous Chloride —Ditertiary Phosphine— Triethylaluminum[*1]

Teruhiko KAGAWA, Yoshio INOUE and Harukichi HASHIMOTO

Department of Synthetic Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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There are some reactions catalyzed by the transition metal catalyst in which the coordinated ligand plays an important role. This investigation has been carried out in order to find out the role of the ligand. The co-dimerization of butadiene and ethylene catalyzed by $CoCl_2$-ditertiary phosphine-$AlEt_3$[1a-e] was chosen for the study. Using ditertiary phosphine, $Ph_2P(CH_2)_nPPh_2$ ($n=1,2,3,4,5,10$) and $Ph_2P(CH_2)_mO(CH_2)_mPPh_2$ ($m=1,2$) as the ligand, the effects of the length of methylene chain between two phosphorus atoms and the ether bond have been investigated.

Experimental

Reagents. Toluene was purified by the usual method and distilled under an atmosphere of nitrogen. Triethylaluminum (Ethyl Corp., U.S.A.) was used without further purification. Butadiene was dried by passing through a column of anhydrous calcium chloride and condensed in a measuring vessel in a dry ice-methanol bath in order to measure its volume. Anhydrous cobaltous chloride and triphenylphosphine were obtained commercially. The preparation of ditertiary phosphines ($Ph_2P(CH_2)_nPPh_2$ and $Ph_2P(CH_2)_mO(CH_2)_mPPh_2$) were performed by the method described by Hewertson and Watson.[2] The purity was confirmed by elementary analysis and melting point. The cobalt complexes of ditertiary phosphine were obtained by the reaction of anhydrous cobaltous chloride with ditertiary phosphines in appropriate solvents, and used for experiments after recrystallization.[3]

Procedure. A 100 m*l* stainless steel autoclave equipped with a magnetic stirrer was charged with calculated amounts of cobalt complex, toluene, butadiene and triethylaluminum in this order under a nitrogen atmosphere. Temperature was then raised to 80—90°C, and ethylene was injected to a pressure of approximately 50 kg/cm^2 and the reaction was carried out with agitation under a constant ethylene pressure. After 2 or 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 gaschromatography.

Result snd Discussion

The co-dimerization products of butadiene and ethylene catalyzed by the cobalt catalyst are mainly 1,4-*cis*-hexadiene and a small amount of 1,3-hexadiene and 2,4-hexadiene. Among these products 2,4-hexadiene is formed by the isomerization of 1,4-hexadiene at higher temperature.[1f]

The effects of the length of methylene chain between two phosphorus atoms in the ditertiary phosphine are shown in Fig. 1. Complexes $CoCl_2(Ph_2P(CH_2)_nPPh_2)$ ($n=3,4$) were found to show the most selective catalytic action for the formation of 1,4-*cis*-hexadiene. In the case of $n=1,5,10$,

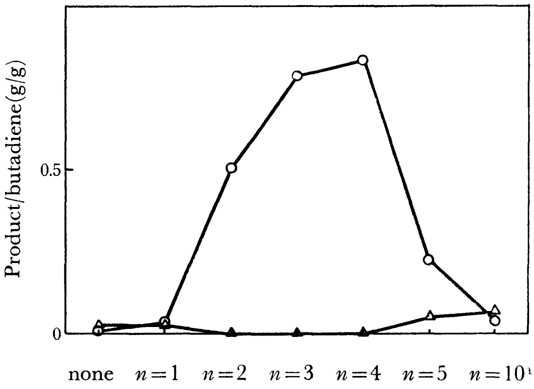

Fig. 1. Effect of the length of methylene chain in catalyst of $CoCl_2(Ph_2P(CH_2)nPPh_2)$-$AlEt_3$ reaction condition: see footnote a) in Table 1, Al/Co=8—10

a) mixture ○ 1,3-hexadiene
△ 1,4-hexadiene

[*1] Ligand Effects. I.

1) *e. g.* co-oligomerization of ethylene and butadiene. a) M. Iwamoto and S. Yuguchi, This Bulletin, **39**, 2001 (1966). b) M. Iwamoto and S. Yuguchi, *J. Org. Chem.*, **31**, 4290 (1966). c) M. Iwamoto and S. Yuguchi, This Bulletin, **41**, 150 (1968). d) M. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **70**, 1221, 1505 (1967). e) M. Iwamoto and S. Yuguchi, *ibid.*, **71**, 133, 233, 237, (1968). f) G. Hata, This Bulletin, **41**, 2443, 2762 (1968).

2) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.

3) a) W. Dew. Horrockes, Jr., G. R. Van Hecke and D. Dew. Hall, *Inorg. Chem.*, **6**, 694 (1967). b) L. Sacconi and J. Gelsomini, *ibid.*, **7**, 291 (1968).

Table 1. Effect of Al/Co ratio[a)]

Complex mmol	Al/Co	Butadiene g	1,4-HD[b)] g	2,4-HD g	1,3-HD g
$CoCl_2(DPP)$	2.0	36.4	none	none	none
0.295	4.7	34.2	38.0	none	none
	8.9	32.4	38.3	none	none
	24.8	30.6	30.8	trace	none
$CoCl_2(DPE)_2$					
1.00	7.3	35.3	18.1	trace	none
$CoCl_2(DPE)$					
1.00	7.7	37.8	19.1	2.7	trace
0.50	11.0	31.2	4.0	trace	2.09[c)]

a) reaction temperature ~80°C,
reaction time 2 hr
$P_{C_2H_4}=50$ kg/cm^2
b) HD=hexadiene
c) 8.3 g of 3-methyl-1,4,6-heptatriene was also produced.

the amount of 1,4-hexadiene decreased and that of 1,3-hexadiene increased and the products distribution became similar to that of $CoCl_2$-$AlEt_3$ catalyst. It seems that the above selectivity is partly due to the adequate stabilization of the active intermediate by the formation of six or seven membered chelate ring which consists of metal and ditertiary phosphine. However, the bulkiness of the ligand may also influence the selectivity of the products.

$CoCl_2(DPE)$*[2] and $CoCl_2(DPE)_2$ had the same activity at a low concentration of triethylaluminum, but at the molar ratio of Al/Co=11, $CoCl_2(DPE)$ lost the selectivity of 1,4-hexadiene as is given in Table 1. From a structural point of view, the complex $CoCl_2(DPE)$ has a tetrahedral structure, and $CoCl_2(DPE)_2$ is considered to be five coordinated complex.[3a)] However, $CoCl_2(DPP)$*[3] which has the same structure as $CoCl_2(DPE)$[3b)] was a good catalyst for 1,4-hexadiene formation in a wide range of the molar ratio of Al/Co.*[4] It may be shown that the activity does not depend on the initial structure of the complex. The structure of reaction intermediates seems to be different. Further addition of DPE to $CoCl_2DPE$ with molar ratio of DPE/$CoCl_2(DPE)$ = 1.0, did not change the yield of 1,4-hexadiene appreciably. When DPE was added to the $CoCl_2(DPE)_2$, the result was similar to that of $CoCl_2(DPE)_2$ alone. Thus the additional DPE may not disturb 1,4-hexadiene formation by occupying the active site of the metal

When $Ph_2P(CH_2)_mO(CH_2)_mPPh_2$ was used as a ligand, the selectivity of 1,4-hexadiene was small and the high boiling point products were produced. The product distribution depended on the reaction temperature; at lower temperatures 1,3-hexadiene and butadiene dimerization product *i. e.* 3-methyl-1,4,6-heptatriene were mainly formed, and at higher temperatures 1,4-hexadiene and 2,4-hexadiene. The catalyst $CoCl_2DPMO$*[5] was active at 50°C. However, in the case of $CoCl_2DPEO$*[6] the activity appeared over 120°C. If we compare the number of atoms between two phosphorus atoms of DPMO with that of DPP, the length of the ligand is of the same order, but the catalytic activity and the selectivity are extremely different. Thus the electronic effect of the oxygen atom in the ether bond can not be neglected.

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*[2] DPE=1,2-bis(diphenylphosphino)ethane
*[3] DPP=1,3-bis(diphenylphosphino)propane
*[4] see Table 1.
*[5] DPMO=bis(1-diphenylphosphinomethyl) oxide
*[6] DPEO=bis(2-diphenylphosphinoethyl) oxide