

Note

Dimerization and Oligomerization of Ethylene Catalyzed by a Palladium(II) Complex with Imine-phosphine Ligand

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The palladium-iminophosphine complex $[\text{Pd}(\text{P-N})(\text{CH}_3)\text{Cl}]$ ($\text{P-N} = o\text{-diphenyl-phosphino-}N\text{-benzaldimine}$) has been found to be a catalyst for dimerization and trimerization of ethylene. Some mechanistic insight concerning this oligomerization is discussed.

INTRODUCTION

Transition-metal catalyzed dimerization and oligomerization of ethylene or propylene are well documented.¹ Among the known cases, palladium complexes are generally less used presumably due to their relatively low reactivity. However, palladium chloride has been known to be a catalyst for dimerization of ethylene in various solvents.² In a kinetic study, Brookhart and coworkers suggested that the activation energy of the ethylene insertion into a Pd-C bond of $[(\text{N-N})\text{PdR}]^+$ is ca. 19 kcal/mol, which may be easily accessed under mild conditions.³ Indeed, dimerization of ethylene catalyzed by $(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2$ and $[(\eta^3\text{-allyl})\text{Pd}(\text{P-O})]^+$ has been reported recently.^{4,5} This outcome indicates the importance of ligand effect.

Recently, ligands of mixed donors of phosphorus and nitrogen have received much attention; particularly those with imino donor are thought to have strong *trans*-influence.⁵ Such complexes can lead to stoichiometric olefin and CO insertion. To understand the ligand effect in alkene oligomerization, we report the results of $[\text{Pd}(\text{P-N})(\text{CH}_3)\text{Cl}]$ [P-N : phosphino-imino ligand] catalyzed dimerization of ethylene.

RESULTS AND DISCUSSION

The imine-phosphine palladium complex $[\text{Pd}(\text{P-N})(\text{CH}_3)\text{Cl}]$ **1** ($\text{P-N} = o\text{-diphenylphosphino-}N\text{-benzaldimine}$)⁶ does not help the reactions of ethylene polymerization, but is an excellent catalyst for dimerization of ethylene. In the typical run, in a 600 mL autoclave was placed complex **1** (0.02 mmol) as well as sodium tetrakis[3,5-di(trifluoromethyl)phenyl]borate (0.02 mmol) in dichloromethane (50 mL) and then pressured with ethylene. During the reaction course, ethylene was refilled when the pressure was found to drop. After

the pressure stopped changing, the reaction products were distilled and trapped at -78°C . The analysis was done by ^1H NMR spectroscopy. The results of the oligomerization of ethylene are summarized in Table 1.

In all instances, only 1-butene and 1-hexene were produced. It is worth noting that the formation of any other isomeric species (e.g., 2-butene) or longer carbon chain alkenes was not observed. When the reactions were carried out under higher pressure (entries 1-3), the relative yields of 1-hexene versus 1-butene increase along with the decrease of overall conversion. As to the solvent effect, a greater selection for 1-butene over 1-hexene is observed in aromatic solvents than in dichloromethane, although the overall conversions are still worse. The same is true of higher temperatures.

We deliberately examined the reaction of mixing 1-butene and ethylene as the starting material, but only 1-butene was recovered. There was no observation of any product of co-dimerization or dimerization of 1-butene. While 1-butene was employed as the sole reactant, isomerization was found to take place, resulting in the formation of 2-butenes.

In contrast to the diimine-palladium complexes which are known to catalyze the polymerization of various olefins, the imine-phosphine complex developed in this study is suitable for oligomerization of ethylene. A possible reaction pathway is proposed in Scheme I. The sodium tetraarylborate would generate a species **I** with unsaturated coordination at the palladium(II) center. Ethylene-insertion followed by β -elimination could result in the unsaturated complex of metal hydride **II** which is believed to be responsible for the dimerization and trimerization of ethylene.

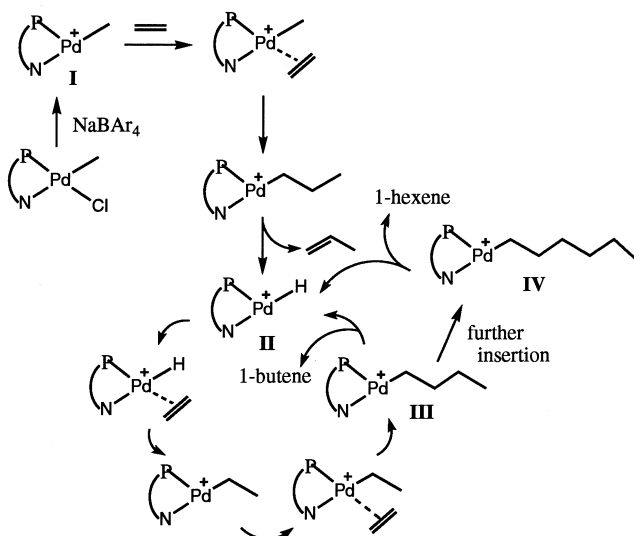
Two aspects concerning the catalytic activity on the imine-phosphino complex of palladium(II) are noteworthy. First of all, although the complex is able to catalyze the isomerization of 1-butene to 2-butene, this process has not been found in the dimerization process. Secondly, the forma-

Table 1. Oligomerization of Ethylene Catalyzed by Pd(P-N)MeCl

Pressure of CH ₂ =CH ₂ (psi)	solvent	T(°C)	Time (h)	Product	Turnover no. x 10 ³
80	CH ₂ Cl ₂	rt	72	butene (0.928 mol); 1-hexene (0.266 mol)	46.4 13.6
200	CH ₂ Cl ₂	rt	12	1-butene (0.176 mol); 1-hexene (0.049 mol)	8.80 2.45
400	CH ₂ Cl ₂	rt	12	1-butene (0.125 mol); 1-hexene (0.025 mol)	6.30 1.30
80	C ₆ H ₆	rt	72	1-butene (0.649 mol); 1-hexene (0.137mol)	32.5 6.85
80	CH ₂ Cl ₂	60°C	48	1-butene (0.103 mol); 1-hexene (0.02 mol)	5.20 1.0
400	C ₆ H ₆	rt	48	1-butene (0.155 mol); 1-hexene (0.016 mol)	7.8 0.8
80	C ₆ H ₅ CH ₃	rt	72	1-butene (0.183 mol); 1-hexene (0.029 mol)	9.2 1.5

Experimental Procedure: Into an autoclave(600mL) was placed Pd(P-N)MeCl (0.02 mmol) and NaBAR₄ (Ar = 3,5-(CF₃)₂C₆H₃) (0.02 mmol) in dried solvent. Ethylene gas was pressured. The mixture was stirred for a period of time and the reaction products were analyzed spectroscopically.

Scheme I Reaction pathway for oligomerization



tion of higher olefins beyond 1-butene was lacking. It indicates that either the coordination of ethylene is probably overwhelming other α -olefins or insertion of a high olefin is slow in such a system.

EXPERIMENTAL SECTION

General Information

Nuclear magnetic resonance spectra were recorded in

CDCl₃ on either a Bruker AC-E 200 or AM-300 spectrometer. All of the reaction, manipulation, and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. All chemicals and solvents were used from commercial sources without further purification. Pd(P-N)MeCl was prepared according to the procedure previously reported.⁶

Procedure for Dimerization

Into an autoclave (600 mL) was placed Pd(P-N)MeCl (0.02 mmol) and NaBAR₄ (Ar = 3,5-(CF₃)₂C₆H₃) (0.02 mmol) in dried solvent. Upon flash with ethylene gas several times, ethylene gas was loaded. During the reaction, ethylene was re-filled when the pressure was found to drop. The mixture was stirred for a period of time and the reaction products were analyzed spectroscopically.

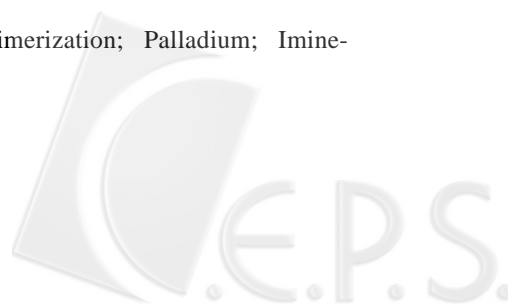
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Key Words

Ethylene; Dimerization; Palladium; Imine-phosphine.



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