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ENHANCEMENT BY WATER OF THE ACTIVITY OF σ-ARYL PALLADIUM(II) CATALYST FOR CODIMERIZATION OF ETHYLENE WITH STYRENE

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A catalytic amount of water has been found to increase significantly the activity of the catalyst system composed of bis(triphenylphosphine)σ-aryl(halo)palladium(II) and trifluoro boron etherate for the codimerization of ethylene with styrene to give 3-phenyl-1-butene.

In the previous papers, it was shown that trans-bis(triphenylphosphine)σ-aryl(halo)nickel(II) compound effectively catalyzes ethylene dimerization[1) and its codimerization with styrene in the presence of trifluoro boron etherate in methylene chloride.[2) The research of this catalyst system was extended to trans-bis(triphenylphosphine)σ-aryl(halo)palladium(II) compound, which has exactly the same structure as that of the nickel(II) compound,[3) to compare their catalytic activities. The σ-phenyl palladium(II) catalyst system was much less active for ethylene dimerization under normal temperature and pressure even in the presence of a large amount of trifluoro boron etherate, whereas a considerable amount of phenyl ligand was consumed for the phenylation of ethylene to give styrene and its codimer with ethylene. All attempts to activate the palladium(II) catalyst system for the codimerization of ethylene with styrene in well dry solvents were unsuccessful. The yield of the codimer, however, is effectively increased by adding a catalytic amount of water as represented in Table 1, where no appreciable increase in the amount of butenes was observed. The addition of excess amounts of water in moles more than that of trifluoro boron etherate definitely lowered the yield of the codimers. In the product, only trace amount of 2-phenyl-2-butene was detected despite the formation of 3-methyl-3-phenyl-1-pentene, which should be formed from the codimerization of ethylene with 2-phenyl-2-butene. These codimers are also obtained by σ-aryl nickel(II) catalyst system,[2) but not by palladium dichloride catalysts in the absence of Lewis acid.[4) Neither methanol nor phenol was so effective. The addition of dry hydrogen chloride also gave no codimer, and the phenyl ligand of the palladium(II) compound was almost quantitatively cleaved to give benzene.

From the NMR chemical shift, no appreciable interaction of water(1.5~1.6 ppm) with the palladium(II) compound was observed in methylene chloride alone. In the presence of trifluoro boron etherate, however, the absorption due to water shifted

Table 1. Effect of water on the yield of codimer of ethylene with styrene

$C_6H_5Pd(P\Phi_3)_2X$ (0.4 mmol)	Additives (mmol)		Time (hr)	3-p-1-b[a] (mmol)	3-m-3-p-1-b[b] (mmol)	Total codimer (mmol)
X = Br	H_2O	0	3	trace	none	trace
X = Br	H_2O	1.2	3	2.0	0.16	2.16
X = Br	H_2O	1.6	3	3.1	0.28	3.38
X = Br	H_2O	2.0	3	2.4	0.17	2.57
X = Br	CH_3OH	1.6	3	0.15	trace	0.15
X = Br	C_6H_5OH	1.6	3	0.12	trace	0.12
X = I	H_2O	0	2	trace	none	trace
X = I	H_2O	0.8	2	3.3	0.48	3.78
X = I	H_2O	1.6	2	3.7	0.95	4.65
X = I	H_2O	2.4	2	3.3	0.35	3.65

a) 3-phenyl-1-butene, b) 3-methyl-3-phenyl-1-pentene.

to a much lower field(9~11 ppm) with broadening, which depended not only on the temperature, but also on the mole ratio of water to trifluoro boron etherate, and the free ether(CH_2 3.72(q) ppm, CH_3 1.30(t) ppm) could be distinguished at -20 °C from trifluoro boron etherate(CH_2 4.31(q) ppm, CH_3 1.46(t) ppm) without any other new absorption having been detected. The relative intensities of NMR absorptions were in conformity with the equilibrium: $H_2O + BF_3OEt_2 \rightleftharpoons BF_3H_2O + OEt_2$, although the absorption due to the free water could not be separated from BF_3H_2O even at -60 °C probably because of a rapid proton exchange between them. At present, the role of water has not been elucidated yet, however, the enhancement by water was also observed in the σ-aryl nickel(II) compound catalyst system for the codimerization of ethylene with styrene or butadiene. This suggests that water has an essential role in the olefin dimerization catalyzed by these catalyst.

All the experiments were carried out under nitrogen atmosphere. To a solution of bis(triphenylphosphine)σ-phenyl(bromo)palladium(II)(0.4 mmol)[3] in dry methylene chloride(30 ml) in a 50 ml flask were added trifluoro boron etherate(2.4 mmol), water and styrene(8.7 mmol) in this order. The nitrogen gas in the flask had been evacuated at the temperature of liquid nitrogen before dry ethylene gas was introduced(760 mmHg at 0 °C). The flask was left to warm to room temperature for 3 hr. The reaction was terminated by adding an aqueous sodium hydroxide solution. Most of the volatile substances such as ethylene, butenes, and the solvent were transferred into another flask by means of a liquid nitrogen trap before non-volatile materials were quantitatively determined by gaschromatography.

Reference

1) K. Maruya, T. Mizoroki, and A. Ozaki, Bull. Chem. Soc. Japan, 45, 2255(1972).
2) N. Kawata, K. Maruya, T. Mizoroki, and A. Ozaki, ibid, 44, 3217(1971).
3) P.Fitton and E. A. Rick, J. Organometal. Chem., 28, 287(1971).
4) K. Kawamoto, A. Tatani, T. Imanaka, and S. Teranishi, Bull. Chem. Soc. Japan, 44, 1239(1971).

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