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SELECTIVE DIMERIZATION OF ETHYLENE CATALYZED BY HALOGENOTRIS(TRIPHENYLPHOSPHINE)COBALT(I)-BORON TRIFLUORIDE ETHERATE IN HALOBENZENE

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Dimerization of ethylene is very selectively catalyzed by halogenotris(triphenylphosphine)cobalt(I) in the presence of Lewis acid in halobenzene. The catalytic activity is significantly affected by the solvent, bromobenzene being most effective.

Halogenotris(triphenylphosphine)cobalt(I) complex[1)] prepared from cobalt(II)-halide, triphenylphosphine, and zinc metal in alcohol, is known to slowly catalyze cyclodimerization[2)] of butadiene to 1,5-cyclooctadiene and 4-vinyl-1-cyclohexene at 60 °C, and hydrodimerization[3)] of acrylic esters in alcohol, while no activity for ethylene dimerization[4)] is known with the cobalt(I) complex. We found that in the presence of Lewis acid, particularly boron trifluoride etherate in halobenzene, the cobalt(I) complex catalyzes the dimerization of ethylene to butenes under a mild condition with an activity comparable to that of cobalt(III)acetylacetonate-triethylaluminium[5)] or hydridodinitrogentris(triphenylphosphine)cobalt(I).[6)]

A typical experimental procedure was as follows. All operation was carried out under nitrogen atmosphere. To a dry halobenzene solution (10 ml) of halogenotris-(triphenylphosphine)cobalt(I) (0.1 mmol) in a two necked flask (50 ml) was added boron trifluoride etherate (0.48 mmol). The nitrogen gas in the flask was evacuated at liquid nitrogen temperature before introduction of ethylene gas (734 mmHg) at 0 °C with continuous supply of ethylene to keep the pressure constant. The reaction was, then, terminated by adding aqueous sodium hydroxide solution (1N, 3 ml). The amounts of butenes formed were quantitatively determined by gas chromatography.

Ethylene dimerization with this catalyst system took place almost quantitatively (99.8 %) at 0 °C under atmospheric pressure after an induction period (~5 min). Only a trace amount of hexene (~0.2 %) was detected in the products. Consistently the catalyst is inactive for dimerization of propylene or butene.

The catalytic activity was found to be remarkably affected by the solvent (Table). Bromobenzene is most effective among the solvents tested and the effectiveness sequence of solvents is as follows; bromobenzene>iodobenzene>o-dichlorobenzene>chlorobenzene>o-chlorotoluene. No dimerization was detected in benzene, ethylbromide, allylbromide, benzylbromide, dichloromethane, tetrahydrofuran, benzonitrile, and anisole. When benzene or anisole was used as the solvent, a black precipitate was formed on addition of boron trifluoride etherate, and the color of solution changed from olive-green to greenish-blue. This seems to be caused by decomposition of the cobalt complex according

Table. Dimerization of Ethylene Catalyzed by $CoX(PPh_3)_3$

Cat. X	Solvent (ml)	Lewis acid (mmol)	Rate of C_2' absorption (ml/min)	Amount of C_2' absorbed (mmol)	C_4' distribution (%)		
					$1-C_4'$	$t-2-C_4'$	$c-2-C_4'$
Cl	C_6H_5Cl	BF_3OEt_2(0.48mmol)	0.87	1.4	78	10	11
Cl	C_6H_5Br	BF_3OEt_2(0.48mmol)	15	16	12	46	42
Cl	C_6H_5I	BF_3OEt_2(0.48mmol)	8.1	10	20	39	41
Cl	o-$C_6H_4Cl_2$	BF_3OEt_2(0.48mmol)	1.9	2.1	47	23	31
Cl	o-$CH_3C_6H_4Cl$	BF_3OEt_2(0.48mmol)	0.18	0.78[a)]	85	6.4	8.3
Br	C_6H_5Br	BF_3OEt_2(0.48mmol)	12	12	14	46	40
I	C_6H_5Br	BF_3OEt_2(0.48mmol)	12	11	21	41	38
Br	C_6H_5Br	$AlCl_3$ (0.083mmol)	13	16[a)]	7.5	53	40
Br	C_6H_5Br	$AlBr_3$[b)] (0.51mmol)	1.9	1.9	53	33	14

$CoX(PPh_3)_3$ 0.1 mmol, Solvent 10 ml, Temp. 0 °C, and Time 30 min.
a) Time 60 min. b) Suspended.

to the equation: $2CoX(PPh_3)_3 = CoX_2(PPh_3)_2 + Co + 4PPh_3$, $Ph=C_6H_5$.

The catalyst was also completely deactivated by addition of a small amount (0.5ml) of alkyl halide such as benzylbromide, allylbromide, and ethylbromide to the bromobenzene solution (10 ml) with the color of solution being changed from olive-green to blue.

Addition of triphenylphosphine was found to retard the dimerization, whereas a catalytic amount of water ($H_2O/Co \geq 1$) completely deactivated the catalyst. This result is substantially different from that observed with bis(triphenylphosphine)σ-arylnickel (II)bromide-boron trifluoride etherate system, where a trace amount of water significantly enhanced the catalytic activity for the dimerization of ethylene and its codimerization with styrene[7)] or butadiene.[8)]

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