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Selective Dimerization of Ethylene Catalyzed by Halogenotris(triphenylphosphine)cobalt(I) Complex-Lewis Acid

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Dimerization of ethylene is highly selectively catalyzed by $CoX(PPh_3)_3$ (X=Cl, Br, and I) in the presence of Lewis acid in halobenzene under mild conditions. The catalytic activity is significantly affected by the solvent, bromobenzene being the most effective. The role of $BF_3 \cdot OEt_2$ seems to be formation of a one-to-one complex of Co(I) and BF_3, since the rate of ethylene dimerization attains a plateau on addition of equimolar amount of $BF_3 \cdot OEt_2$. The isomerization of 1-pentene is enhanced by addition of molecular hydrogen or ethylene to the catalyst system. The isotopic scrambling between C_2H_4 and C_2D_4 takes place faster than dimerization. The results are in line with hydridocobalt intermediate formed by the oxidative addition of ethylene to Co(I) complex.

Many papers have appeared on the ethylene dimerization catalyzed by nickel catalysts,[1)] but fewer examples are known of cobalt catalysts for the same reaction: *i.e.*, cobalt oxide–charcoal[2)] as a heterogeneous catalyst, homogeneously soluble hydridodinitrogentris(triphenylphosphine)cobalt(I) complex,[3)] and cobalt(II) compounds[4)] activated with alkylaluminium compounds as the reducing agent.

During a study of the role of Lewis acid in the activation of olefin with cobalt complexes, it was found that halogenotris(triphenylphosphine)cobalt(I) is also fairly active and selective in giving ethylene dimer in the presence of Lewis acid such as $BF_3 \cdot OEt_2$ or $AlCl_3$ in halobenzene at ambient temperature and pressure,[5)] but it has no activity at all for propylene dimerization, a unique feature of this catalyst system.

This paper reports the properties of this catalyst system in detail.

Experimental

Materials. Halogenotris(triphenylphosphine)cobalt(I) complexes and bromotris(diphenylmethylphosphine)cobalt(I) complex were synthesized according to the method of Sacco.[6)] The complexes were also obtained by another method. $AlEt_2(OEt)$ (16 ml) was added to the ether solution (200 ml) of $Co(acac)_2$ (39 mmol) and PPh_3 (156 mmol) under nitrogen atmosphere at 0 °C, followed by addition of halobenzene. A green precipitate was formed in a few minutes. The precipitate dried in a vacuum was identified to be halogenotris(triphenylphosphine)cobalt(I) complex by elemental analysis, IR, magenetic susceptibility, and several chemical reactions. The result of elemental analysis of cobalt(I) complex is shown in Table 1.

Trace amounts of water and air in ethylene gas were excluded by vacuum distillation. Solvents were dried by P_2O_5 (halobenzene) or metallic sodium(benzene and ether), and distilled under nitrogen atmosphere. $BF_3 \cdot OEt_2$ was also purified by distillation. $AlCl_3$ was purified by sublimation at 200 °C in nitrogen atmosphere. Other commercial Lewis acids, such as $AlBr_3$, $SnCl_2$, $SnCl_4$, and $TiCl_4$ were used, without purification. Hydrogen gas was deoxidized by passing through a Pd–Al_2O_3 pellet at 90 °C and dried with a liquid nitrogen trap.

Procedure. To one of the cobalt(I) complexes placed in a two necked flask(50 ml), were added solvent and $BF_3 \cdot OEt_2$ with stirring under nitrogen atomosphere. The nitrogen gas in the flask was evacuated at liquid nitrogen temperature, before ethylene was introduced. The rate of ethylene absorption was measured at constant temperature and pressure by means of a gas burette. The reaction was terminated by addition of an aqueous solution of NaOH, the products being analyzed by GLC.

Isotopic exchange of C_2H_4–C_2D_4, dimerization of C_2D_4, and isomerization of 1-alkene were performed by analogous procedures. Isotopic mixtures of butenes and ethylene were analyzed by mass spectrometry with an ionization potential of 10 eV.

Results and Discussions

Effect of Solvent on Catalytic Activity. The catalytic activity of $CoX(PPh_3)_3$–$BF_3 \cdot OEt_2$ for ethylene dimerization was determined in various solvents (Table 2). Ethylene was absorbed readily in halobenzene solvents, whereas no absorption was observed in other solvents including benzene, anisole, tetrahydrofran, benzonitrile, ethyl bromide, propyl bromide, benzyl bromide, and dichloromethane. Bromobenzene was the most effective solvent among halobenzenes and the rate of ethylene absorption decreased in the order, bromobenzene > iodobenzene > *o*-dichlorobenzene > chlorobenzene > *o*-chlorotoluene. The color of halobenzene solutions of bromotris(triphenylphosphine)cobalt(I) turned

Table 1. Elemental analysis

	Found[a)]			Found[b)]			Calcd		
	C (%)	H (%)	X (%)	C (%)	H (%)	X (%)	C (%)	H (%)	X (%)
$CoCl(PPh_3)_3$	72.7	5.7	4.2	72.1	5.2	3.9	73.6	5.2	4.0
$CoBr(PPh_3)_3$	69.6	5.5	8.6	70.4	5.2	9.9	70.1	4.9	8.6
$CoI(PPh_3)_3$	66.2	5.2	12.7				66.7	4.7	13.1
$CoBr(PPh_2Me)_3$	63.3	5.5	10.6				63.3	5.3	10.8

a) The method of Sacco. b) The method described herein.

TABLE 2. DIMERIZATION OF ETHYLENE CATALYZED BY $CoX(PPh_3)_3$
$CoX(PPh_3)_3$ 0.1 mmol, $BF_3 \cdot OEt_2$ 0.48 mmol, Solvent 10 ml, Temp 0 °C, and Time 30 min.

Cat. X	Solvent (ml)	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	0.87	1.4	78	10	11
Cl	C_6H_5Br	15	16	12	46	42
Cl	C_6H_5I	8.1	10	20	39	41
Cl	o-$C_6H_4Cl_2$	1.9	2.1	47	23	31
Cl	o-$CH_3C_6H_4Cl$	0.18	0.78a)	85	6.4	8.3
Br	C_6H_5Cl	0.55	0.56	90	4.9	5.5
Br	C_6H_5Br	12	12	14	46	40
Br	C_6H_5I	2.1	2.8	53	22	26
Br	o-$C_6H_4Cl_2$	1.8	1.9	50	21	29
Br	o-$CH_3C_6H_4Cl$	0.07	0.35b)	90	4.6	5.6
I	C_6H_5Cl	0.31	0.40	81	6.1	13
I	C_6H_5Br	12	11	21	41	38
I	C_6H_5I	0	0	—	—	—
I	o-$C_6H_4Cl_2$	2.1	2.7	42	22	36
I	o-$CH_3C_6H_4Cl$	0.25	0.50	70	7.9	22
Brc)	C_6H_5Br	1.5	1.7	4.9	62	33

a) Time 60 min. b) Time 120 min. c) $CoBr(PPh_2Me)_3$ was used.

from pale green to deep green on addition of $BF_3 \cdot OEt_2$. In benzene or anisole, however, the color of the solution turned gradually to greenish blue with a black precipitate. The following disproportionation seems to take place readily in benzene or anisole.

$$2CoBr(PPh_3)_3 \longrightarrow CoBr_2(PPh_3)_2 + 4PPh_3 + Co$$

On the other hand, $CoBr(PPh_3)_3$ reacts with alkyl halides to give Co(II) complex and quaternary phosphonium salts. Accordingly the $CoX(PPh_3)_3$ activated with $BF_3 \cdot OEt_2$ could act as a catalyst only in halobenzene for the ethylene dimerization.

When ethylene gas was introduced immediately after the addition of $BF_3 \cdot OEt_2$, a high rate of ethylene dimerization was attained. However, when the $CoBr(PPh_3)_3$–$BF_3 \cdot OEt_2$ mixture was left standing for 40 min without introducing ethylene, a trace amount of black precipitate was formed, resulting in complete deactivation of the catalyst for ethylene dimerization. It seems likely that the activated form of the catalyst is stabilized by the presence of ethylene as well as halobenzene.

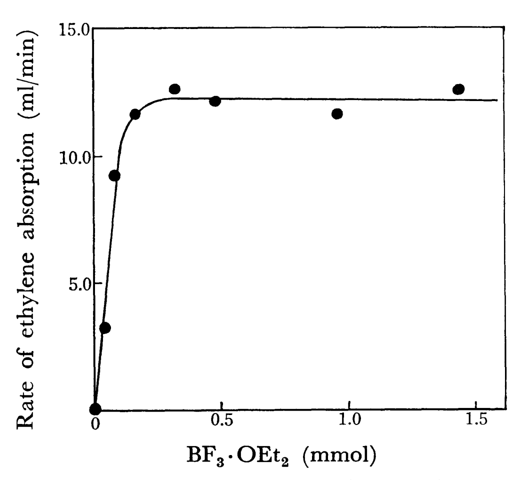

Fig. 1. Rate of ethylene absorption *vs.* the amount of $BF_3 \cdot OEt_2$ added.
$CoBr(PPh_3)_3$ 0.1 mmol, PhBr 10 ml, $P_{C_2'}$ 734 mmHg, and 0 °C.

Effects of Lewis Acid and Cobalt(I) Complex Concentration. As shown in Fig. 1, the rate increases linearly with increase in $BF_3 \cdot OEt_2$ concentration up to $BF_3 \cdot OEt_2/CoBr(PPh_3)_3 = 1$, where it attains a plateau value, while in the case of σ-arylNiBr$(PPh_3)_2$ the rate increases until the ratio $BF_3 \cdot OEt_2/\sigma$-arylNiBr$(PPh_3)_2$ exceeds unity.7) The result suggests that there is a strong one-to-one interaction between $CoBr(PPh_3)_3$ and $BF_3 \cdot OEt_2$ such as $CoBr(PPh_3)_3 + BF_3 \cdot OEt_2 \rightarrow [Co(PPh_3)_3]^+[BF_3Br]^-$.

The rate of ethylene dimerization is proportional to the $CoBr(PPh_3)_3$ concentration with a constant ratio of $BF_3 \cdot OEt_2$ to $CoBr(PPh_3)_3$ as shown in Fig. 2. When $AlCl_3$ was used as a Lewis acid, an induction time

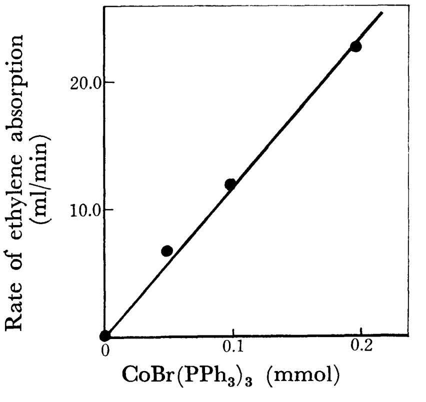

Fig. 2. Rate of ethylene absorption *vs.* the amount of catalyst.
$CoBr(PPh_3)_3/BF_3 \cdot OEt_2$ 1/4.8 (mole ratio), PhBr 10 ml, $P_{C_2'}$ 734 mmHg and 0 °C.

(about 30 min) was observed, which disappeared by pretreatment of $CoBr(PPh_3)_3$ with $AlCl_3$ for 40 min at 0 °C. Since the solubility of $AlCl_3$ is considerably lower than that of $BF_3 \cdot OEt_2$, the induction time can be regarded as the time necessary to activate the Co(I)-complex with $AlCl_3$. No ethylene dimerization was found with the use of other Lewis acids such as $SnCl_2$, $SnCl_4$ and $TiCl_4$.

The addition of $PPh_3(PPh_3/CoBr(PPh_3)_3=3)$ to a $CoBr(PPh_3)_3$–$BF_3 \cdot OEt_2$ (1 : 4.8) catalyst system was found to stop the dimerization almost completely. Water was also found to be a strong inhibitor to cause complete deactivation by addition of equimolar amount of water. $CoBr_2(PPh_3)_2$, $ZnBr_2$, or metallic zinc, which might be a contaminant of $CoBr(PPh_3)_3$ in a trace amount, had no effect on the ethylene dimerization.

Isomerization and Isotopic Scrambling of Olefins. Isomerization of 1-alkene was investigated to elucidate why the present catalyst system is highly specific for ethylene dimerization. As shown in Table 3, neither 1-butene, nor 1-pentene is isomerized. The isomerization of 1-pentene, however, is enhanced in the presence of molecular hydrogen or ethylene. The addition of $BF_3 \cdot OEt_2$ is also essential for the isomerization. The rate of 1-pentene isomerization increases with increase in the amount of ethylene. It seems likely that the active species of the catalyst is a hydridocobalt complex to which the hydrogen is supplied from ethylene or molecular hydrogen, but scarcely from the other olefins. It is evident that ethylene is specifically activated by the present catalyst system.

TABLE 3. ISOMERIZATION OF 1-PENTENE
$CoCl(PPh_3)_3$ 0.1 mmol, $BF_3 \cdot OEt_2$ 0.48 mmol, PhBr 10 ml, 1-C_5' 0.5 ml, 0 °C, and 20 min.

Additives (ml STP)	1-C_5' (%)	*t*-2-C_5' (%)	*c*-2-C_5' (%)
—	99.6	0.1	0.3
C_2' (10)	97.3	1.1	1.6
C_2' (30)	41.5	27.6	30.9
C_2' (100)	18.9	45.0	36.1
H_2 (63)	22.2	23.0	54.8
H_2[a] (80)	99.3	0.6	0.1

a) No $BF_3 \cdot OEt_2$ was added.

The formation of hydridocobalt species during the course of ethylene dimerization is in line with the result for isotopic scrambling in C_2H_4 and C_2D_4 (Table 4). Since the deuterium distribution in the unreacted ethylene attains a value very close to the equilibrium within 13 min, during which the conversion of ethylene to butenes is only 12%, the hydrogen exchange should proceed much faster than ethylene dimerization. The result for the dimerization of C_2D_4, in which the atomic fraction of hydrogen (f_H) is 0.006, indicates that no hydrogen is supplied from any substance other than ethylene, since no appreciable increase in f_H is observed for the unreacted ethylene as well as for the butenes formed (Table 4). The H–D exchange run between C_2D_4 and C_3H_6 shows that the f_H of propylene considerably decrease, while those of produced butenes and unreacted ethylene decrease, indicating that propylene can react with the hydridocobalt species, while it can not be dimerised.

Possible Processes of Formation of Hydridocobalt Species. Olefin dimerization with transition metal complex catalysts is mostly interpreted in terms of transient hydro- and alkyl-complexes. The isomerization of 1-alkene catalyzed by the present catalyst system in the presence of ethylene or hydrogen (Table 3) and isotopic scrambling in ethylene molecules (Table 4) are also explained by hydridocobalt species, for which the hydrogen is supplied from ethylene.

Since the dimerization proceeds specifically in halobenzene solvents, it may be supposed that halobenzene is oxidatively added to the cobalt(I) complex to give a σ-phenylcobalt(III) complex. Ethylene may, then, be inserted into the σ-phenylcobalt(III) complex, followed by elimination of the β-hydrogen to give H–Co(III) species and styrene. This process, however, seems to be unlikely, since neither styrene, its codimer with ethylene, nor benzene was detected. A more likely process is an oxidative addition of ethylene to give H–Co–CH=CH$_2$. Oxidative addition of vinyl compounds such as alkyl methacrylate is verified with ruthenium complex.[8] No increase in f_H of butenes and the residual ethylene in the dimerization using deuterioethylene (Table 4) supports this process for the formation of hydridocobalt species, although we have

TABLE 4. ISOTOPIC EXCHANGE REACTION
$CoCl(PPh_3)_3$ 0.1 mmol, $BF_3 \cdot OEt_2$ 0.48 mmol, PhBr 10 ml, and 0 °C.

C_2D_4 (mmol)	C_2H_4 (mmol)	Time (min)	Sample	D distribution (%)									Con. (%)	f_H
				d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
0.35	0.65		C_2' (int.)	62	0.8	1.4	4.1	32						0.64
0.35	0.65	5	C_2' (resid.)	28	29	27	9	7.1					0	0.65
0.35	0.65	13	C_2' (resid.)	19 (18)	35 (38)	32 (31)	11 (11)	2.0 (2)*					12	0.65
1.0	0		C_2' (init.)	0	0	0	2.5	97.5						0.006
1.0	0	10	C_2' (resid.)	0	0	0	3.8	96.2						0.009
1.0	0	180	C_4' (prod.)	0	0	0	0	0	0	0.7	5.0	94.3	100	0.008
1.0	C_3H_6	20	C_4' (prod.)	0.6	3.0	9.2	18	24	23	14	6.6	1.6	64	0.46
	1.0		C_3' (resid.)	13	26	27	19	10	5.4					0.66
			C_2' (resid.)	23	31	13	14	9						0.61

( )* Equilibrium value.

no direct evidence.

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