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The Insertion Reaction of Isoprene into Metal-Ethyl Bonds in Various Transition-Metal Salt-Ethylaluminum Compound System

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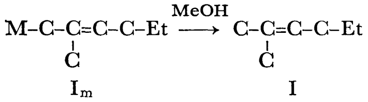
The insertion reaction of isoprene into metal-ethyl bonds in various transition-metal salt (VCl_4, $Fe(AA)_3$, $Co(AA)_2$, $CoCl_2$, $Ni(AA)_2$, or $NiCl_2$-ethylaluminum compound ($AlEt_2Cl$ or $AlEt_3$)) catalyst systems was studied. With the vanadium and the nickel catalysts, 2-methyl-2-hexene and 2-methyl-1-hexene were mainly formed by the methanolysis of the reaction mixture, showing that metal alkenyls, $\mathrm{M{-}C{-}\underset{\substack{|\\ C}}{C}{=}C{-}C{-}Et}$ and $\mathrm{\underset{\substack{|\\ C}}{C}{=}\underset{\substack{|\\ M}}{C}{-}C{-}C{-}Et}$ respectively, are formed in the reaction system. However, in the iron catalyst, only 2-methyl-2,5-hexadiene and 3-methyl-2,5-hexadiene were formed from $\mathrm{M{-}C{-}C{-}C{-}C{=}\overset{\substack{C\\ |}}{C}{-}C}$ and $\mathrm{M{-}C{-}C{-}C{-}\overset{\substack{C\\ |}}{C}{=}C{-}C}$ respectively by the elimination reaction. These results suggest that the stability of metal alkenyls decreases in the order: V≫Ni>Co>Fe.

In a previous paper,[1] the insertion reactions of isoprene into metal-ethyl bonds in the $TiCl_4$-$AlEt_3$ catalyst system were studied, and the relation between the insertion products and the mechanism of the polymerization was discussed.

In the case of a Ziegler-type catalyst, it has been reported[2] that the micro structure of the polymer obtained was affected by the species of the transition metal compound and the organometallic compound. However, up to now the insertion processes of isoprene into a metal-carbon bond in a Ziegler-type catalyst system does not seem to have been discussed sufficiently.

The insertion processes of isoprene into metal-ethyl bonds may be formulated as follows:

1,4-addition:



$$\mathrm{M{-}C{-}\underset{\substack{|\\ C}}{C}{=}C{-}C{-}Et \xrightarrow{MeOH} C{-}\underset{\substack{|\\ C}}{C}{=}C{-}C{-}Et}$$

I_m I

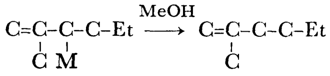
$$\mathrm{Et{-}C{-}\underset{\substack{|\\ C}}{C}{=}C{-}C{-}M \xrightarrow{MeOH} Et{-}C{-}\underset{\substack{|\\ C}}{C}{=}C{-}C}$$

II_m II

3,4-addition:

$$\mathrm{\underset{\substack{|\\ C}}{C}{=}\underset{\substack{|\\ Et}}{C}{-}C{-}C{-}M \xrightarrow{MeOH} \underset{\substack{|\\ C}}{C}{=}\underset{\substack{|\\ Et}}{C}{-}C{-}C}$$

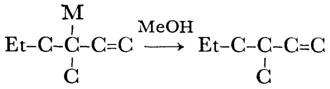
III_m III



$$\mathrm{\underset{\substack{|\\ C}}{C}{=}\underset{\substack{|\\ M}}{C}{-}C{-}C{-}Et \xrightarrow{MeOH} C{=}\underset{\substack{|\\ C}}{C}{-}C{-}C{-}Et}$$

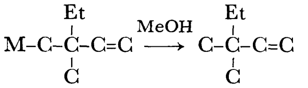
IV_m IV

1,2-addition:



$$\mathrm{Et{-}C{-}\underset{\substack{|\\ C}}{\overset{\substack{M\\ |}}{C}}{-}C{=}C \xrightarrow{MeOH} Et{-}C{-}\underset{\substack{|\\ C}}{C}{-}C{=}C}$$

V_m V



$$\mathrm{M{-}C{-}\underset{\substack{|\\ C}}{\overset{\substack{Et\\ |}}{C}}{-}C{=}C \xrightarrow{MeOH} C{-}\underset{\substack{|\\ C}}{\overset{\substack{Et\\ |}}{C}}{-}C{=}C}$$

VI_m VI

As has been reported in a previous paper,[1] isoprene inserts into metal-ethyl bonds in the $TiCl_4$-$AlEt_3$ catalyst system to give three metal alkenyls, I_m, III_m, and IV_m. In this paper, the insertion reaction of isoprene into metal-ethyl bonds in various transition-metal salt-ethylaluminum systems will be examined in order to establish the influence exerted by the species of the transition-metal compounds.

Experimental

Materials. The ethyl aluminum compounds were obtained from the Ethyl Corporation and were used without further purification.

The isoprene was distilled, deoxygenated by the freeze-thaw method with pumping, and later stored over calcium hydride. The solvent, toluene, was dried over sodium and distilled just before use.

The other reagents used were commercially-available materials.

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[1] Y. Takegami, T. Suzuki and T. Okazaki, *Kogyo Kagaku Zasshi*, **62**, 195 (1967).

[2] C. E. H. Bawn and A. Ledwith, *Quart. Rev.*, **16**, 361 (1962).

Reaction Procedure. A three-necked flask (30 m*l*) was equipped with a magnetic stirrer, a gas inlet, a self-sealing rubber cap, and a gas outlet connected to a mercury manometer and a vacuum system. The gas inlet was connected with a line for argon. Certain amounts of a transition-metal salt, a solvent (toluene), an internal standard (methylcyclohexane), and an ethylaluminum compound were added, in this order, to the reaction flask in an atmosphere of dry argon. The catalyst mixture was aged for five minutes at a certain temperature, and then isoprene (10 mmol) was introduced to start the reaction. After a certain time, the reaction was stopped by adding an excess of methanol containing 10% hydrochloric acid to the reaction mixture. By this treatment the metal alkenyls formed in the system were converted to the corresponding olefinic hydrocarbons. The polymers, if formed, were filtered off, and the organic filtrate was subjected to gas-chromatographic analysis.

A Hitachi model-F6D gas-liquid chromatograph equipped with a hydrogen-flame ionization detector was employed for the quantitative and qualitative analyses of the products. The operating conditions are presented below:

Column	Golay Z45 (SE30)	Golay R45 (PEG)
Size	0.5 mm$\phi \times 45$ m	0.25 mm $\times$ 45 m
Temperature	40°C	50°C
Carrier N_2	0.4 kg/cm^2	0.4 kg/cm^2
Sample size	2 μl	10 μl

Identification of the Products. As standard samples, three C_7 monoolefins, I, III, and IV, were obtained.[1] The isomerization products of 2-methyl-1,5-hexadiene and 3-methyl-1,5-hexadiene were also used for the identification of the C_7 diolefins. This isomerization reaction was carried out with the Co(AA)$_2$-AlEt$_3$ catalyst system.

In the VCl$_4$-AlEt$_3$ AlEt$_2$Cl catalyst system, two products were found; they were identified as I and IV by gas-chromatographic analysis.

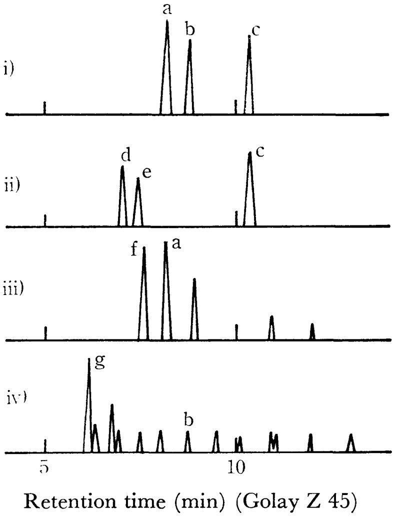

Fig. 1. Retention times of the products in the gas chromatogram.
i) The reaction products in the Fe(AA)$_3$-AlEt$_3$ catalyst system, ii) The hydrogenation products of i), iii) The isomerization products of 2-methyl-1,5-hexadiene, iv) The isomerization products of 3-methyl-1,5-hexadiene
a) 2-methyl-2,5-hexadiene, b) 3-methyl-2,5-hexadiene, c) methylcyclohexane, d) 2-methylhexane, e) 3-methylhexane, f) 2-methyl-1,5-hexadiene, g) 3-methyl-1,5-hexadiene

In the Fe(AA)$_3$ catalyst, two new products, VII and VIII, were found. The structural estimation of VII and VIII was carried out by gas chromatography as follows: a) The relative retention times of VII and VIII in the gas chromatogram were determined (Table 1) and found not to agree with those of the possible monoolefins (I—VI). With the Golay Z-45 column, the relative retention times of VII and VIII were between those of IV and I, but with the Golay R-45 column, those of VII and VIII were larger than those of IV and I.*[1] b) After the hydrogenation of the reaction mix-

Table 1 Relative retention times of the products

Product	Bp (°C)	Relative retention times	
		Golay Z 45(40°C)	Golay R 45(50°C)
III=2,3-Dimethyl-1-pentene	84.3	0.66	0.84
2-Methylhexane	90.1	0.68	—
3-Methylhexane	91.9	0.73	—
XI=3-Methylhexadiene	—	0.75	0.90
IV=2-Methyl-1-hexene	92.0	0.78	0.91
VII=2-Methyl-2,5-hexadiene	91—92.5	0.80	0.95
VIII=3-Methyl-2,5-hexadiene	92.1—92.3[a]	0.83	0.98
I=2-Methyl-2-hexene	95.4	0.87	0.94
XII=3-Methylhexadiene	—	0.91	0.97
Methylcyclohexane	100.9	1.00	1.00
IX=3-Methylhexadiene	—	1.06	1.13
X=2-Methylhexadiene	—	1.13	1.18

a) at 752 mmHg

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*[1] Usually in the Golay R45 column a more polar substance elutes later than a less polar substance.

ture, the peaks of VII and VIII in the gas chromatogram disappeared and those of 2-methylhexane and 3-methylhexane appeared. The relative concentrations of VII and VIII were compared to those of the hydrogenation products, 2-methylhexane and 3-methylhexane (Fig. 1). c) The gas chromatogram of VII and VIII was compared with that of the isomerization products of 2-methyl-1,5-hexadiene or 3-methyl-1,5-hexadiene (Fig. 1). d) According to the literature[3] 2-methyl-2,5-hexadiene and 3-methyl 2,5-hexadiene were synthesized; the gas chromatograms of VII and VIII coincided with those of synthesized samples. From these analyses, and from the relation between the boiling point and the relative retention time, the structures of VII and VIII are considered to be 2-methyl-2,5-hexadiene and 3-methyl-2,5-hexadiene respectively.[*2]

In the cobalt catalyst, seven products were found: they were identified as I, IV, VII, 3-methylhexadienes (IX, XI, and XII), and 2-methylhexadiene (X) by the same method described above.[*3] From their boiling points, IX and X seemed to be conjugated diolenfins.

The nickel catalyst gave four products, I, IV, XI, and XII.

The zirconium, the niobium, and the chronium catalysts gave two products, I and IV.

Results and Discussion

VCl_4-$AlEt_3$ or $AlEt_2Cl$ System. The results are summarized in Table 2 and Fig. 2. The catalyst system immediately became brown-black and homogeneous when $AlEt_3$ or $AlEt_2Cl$ was added to the VCl_4 solution. In this system, 2-methyl-2-hexene (I) and 2-methyl-1-hexene (IV) were formed, showing that two metal alkenyls, I_m and IV_m, are formed. The amounts of these products reached maxima at an early stage and thereafter gradually decreased with an increase in the reaction time.

Table 2 VCl_4-Alkylaluminum system[a)]

Alkyl-aluminum	Temp. (°C)	Time (min)	Products (mol% of VCl_4) IV	I
$AlEt_2Cl$	−70	8	13.7	1.1
	−70	30	12.6	2.8
	−70	60	4.9	1.6
	−30	30	14.4	1.3
	0	30	4.8	2.4
$AlEt_3$	−70	6	4.2	6.0
	−70	30	4.5	3.5
	−70	90	3.3	2.7
	−30	30	2.5	6.0
	0	30	2.8	10.8

a) VCl_4: 1.0 mmol, Alkyl aluminum: 3.0 mmol, Toluene: 10 m*l*, Isoprene: 10 mmol, Catalyst was aged at −70°C for 5 min.

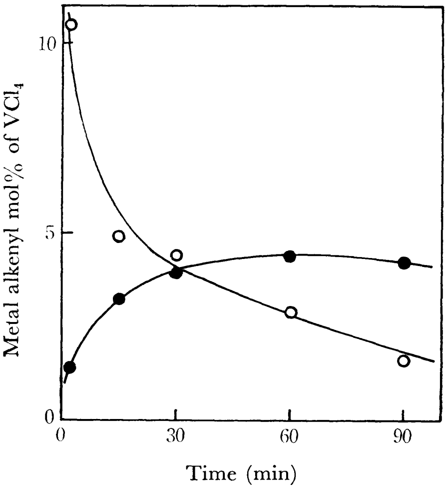

Fig. 2. Isomerization of metal alkenyl with the VCl_4-$AlEt_2Cl$ catalyst system.
Insertion reaction was carried out at −30°C for 10 min, then isoprene remained in the reaction system was pumped off and the reaction system was allowed to stand at 0°C.
○: $\mathrm{C{=}\underset{C}{C}{-}\underset{M}{C}{-}Et}$ (IV_m) ●: $\mathrm{M{-}C{-}\underset{C}{C}{=}C{-}C{-}Et}$ (I_m)

With $AlEt_2Cl$, IV was predominant; this tendency was the more remarkable the lower the temperature. On the other hand, with $AlEt_3$, I was predominant; this tendency was the more remarkable the higher the temperature. Figure 2 shows that IV_m readily isomerizes to I_m at 0°C. This may show that an easy transformation of the $\sigma \rightarrow \pi \rightarrow \sigma$ allyl type has occurred. These results suggest that a lower valence state of vanadium is more favorable for the formation of I_m, and that at lower temperatures IV_m is stable, while at higher temperatures IV_m readily isomerizes to I_m. A small amount of a sticky polymer was always formed. In the vanadium catalyst,

Table 3 $Fe(AA)_3$-$AlEt_3$ system[a)]

Al/Fe	Reaction Temp. (°C)	Time (min)	Products (mol% of $Fe(AA)_3$) VII	VIII
1.0	30	10	2.4	1.7
1.0	30	60	11.5	8.4
1.0	30	120	15.7	11.2
2.0	30	60	8.2	5.3
2.0	0	60	2.0	1.0
5.0	30	120	0	0
2.0[b)]	30	120	0	0

a) Aging temperature: the same temperature as reaction temperature Aging time: 5 min $Fe(AA)_3$: 1.5 mmol
b) $AlEt_2Cl$

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3) M. Iwamoto, Doctral thesis, to Kyoto University.

[*2] These diolefins are considered to be elimination-reaction products from the metal alkenyls in the reaction system, as will be discussed below.

[*3] The structures of the IX—XII diolefins could not be identified more precisely.

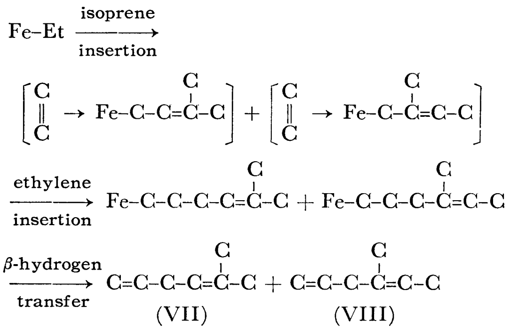
the mode of the insertion reaction was almost the same as that in the titanium catalyst reported on previously.[1]

$Fe(AA)_3$-$AlEt_3$ or $AlEt_2Cl$ System. The results are summarized in Table 3. The catalyst system immediately became brown-black and homogeneous when $AlEt_3$ was added. However, when $AlEt_2Cl$ was added it immediately became dark brown ($AlEt_2Cl/Fe(AA)_3=2$) or milk white ($AlEt_2Cl/Fe(AA)_3=5$) and heterogeneous.

In the case of $AlEt_3$, 2-methyl-2,5-hexadiene (VII) and 3-methyl-2,5-hexadiene (VIII) were formed. On the other hand, no monoolefins was detected in this system. These results suggest that, in the reaction system, the metal alkyls and/or alkenyls are not stable and that diolefins are formed.

One possible process for the formation of the diolefins from the metal alkenyls (I_m—VI_m) is a β-hydrogen transfer of them, with or without a hydride shift. However, this process is considered to give only conjugated and/or allene-type diolefins. Therefore, the selective formation of the isolated diolefins, VII and VIII, cannot be explained in terms of this process.

Hata[4] and Iwamoto[3] have reported that isoprene is co-dimerized with ethylene by the $Fe(AA)_3$-$AlEt_3$ catalyst system under a high pressure of ethylene to give 2-methyl-2,5-hexadiene and 3-methyl-2,5-hexadiene, and that this co-dimerization reaction is probably carried out by the metal hydride. The results obtained in this study are analogous to those obtained by them. However, in this study, even when the gaseous products in the aged mixture were pumped off (−70°C, 15 mmHg, 1 hr), VII and VIII were formed (0.030 and 0.017 mol/mol Fe), shownig that the ethylene is supplied by the iron and/or aluminum complexes having an ethyl bond. From these results, the process of the selective formation of VII and VIII may be formulated as follows:



This insertion reaction is quite different from that in the VCl_4 catalyst.

With $AlEt_2Cl$, no products were detected. This may be because iron-ethyl bonds are not formed in this system, judging from the extraordinary color change.

As for the polymer, it was not formed in every case.

$Co(AA)_2$ or $CoCl_2$-$AlEt_3$ or $AlEt_2Cl$ System. The results are summarized in Table 4. The catalyst system became, either immediately ($Co(AA)_2$) or gradually ($CoCl_2$), brown-black and almost homogeneous when either $AlEt_3$ or $AlEt_2Cl$ was added.

With $AlEt_3$, the I and IV monoolefins and the VII, IX, X, XI, and XII diolefins were formed. The monoolefins are considered to be formed much as in the VCl_4 catalyst. For the formation of these diolefins, two processes are reasonable since, in this case, two conjugated diolefins, IX and X, were also formed. The process which forms the non-conjugated diolefins is the same as in the case of the $Fe(AA)_3$ catalyst. The other process, that which forms the conjugated diolefins, is a β-hydrogen transfer of the metal alkenyls (I_m—VI_m) with or without a hydride shift of them. Therefore, IX and X may be formed by the elimina-

TABLE 4. Co(AA) $CoCl_2$-$AlEt_3$ SYSTEM[a)]

Co salts mmol		Al/Co	Reaction temp. (°C)	Products (mol% of Co salt)						
				XI	IV	VII	I	XII	IX	X
$Co(AA)_2$	1.5	1.0	30[c)]	0.4	0.4	1.3	0.6	0	0	1.6
	1.5	1.0	30	1.6	1.0	4.7	1.1	0	0.9	5.2
	1.5	1.0	30[d)]	2.0	1.1	5.3	1.2	0.4	0.5	4.9
	1.5	2.0	30	0	0.4	0.7	1.5	0	0.5	1.0
	1.5	2.0	0[d)]	0	0.5	0.4	2.2	0	0.6	1.9
	1.5	2.0[b)]	30	0	0	0	0	0	0	0
$CoCl_2$	1.3	2.0	30	0	0	0	0	0	9.0	7.7
	1.5	2.0	0	0	0	0	0.3	0	0.8	1.0

a) The conditions are same as in Table 3, Reaction time: 60 min
b) $AlEt_2Cl$. c) Reaction time: 10 min. d) Reaction time: 120 min

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4) G. Hata, *J. Amer. Chem. Soc.*, **86**, 3903 (1964).

TABLE 5 $Ni(AA)_2$ or $NiCl_2$-ALKYLALUMINUN SYSTEM[a)]

Ni salt	Al/Ni		Reaction Temp. (°C)	Products (mol% of Ni salt)			
				XI	IV	I	XII
$Ni(AA)_2$	1.0	$AlEt_3$	30[b)]	0	1.1	1.1	0
	1.0		30	0	2.0	2.2	0
	1.0		30[c)]	0	3.5	4.6	0
	2.0		30	0	1.0	1.1	0
	2.0		0	0.8	1.8	1.4	0
	2.0	$AlEt_2Cl$	30	0	1.7	3.2	0
	2.0		0	0	0.5	1.4	0
	5.0		30	0	0	0	0
$NiCl_2$	2.0	$AlEt_3$	30	0	0	0	0
	2.0		0[c)]	0.4	0.3	2.6	1.0

a) The conditions are same as in Table 3, Reaction time: 60 min, Ni salt: 1.5 mmol.
b) Reaction time: 10 min. c) Reaction time: 120 min

tion reaction from II_m or V_m, and from I_m or IV_m, respectively.

Especially in the case of the $CoCl_2$ catalyst, the conjugated diolefins, IX and X, were selectively formed at the reaction temperature of 30°C. This result was quite different from that in the $Co(AA)_2$ catalyst, in which the I and IV monoolefins and the VII, XI, and XII diolefins were also formed. This may suggest that, in the $Co(AA)_2$ catalyst, the high reactivity of the metal alkenyls for the isomerization reaction give various products.

A very small amount of an oily yellow polymer was formed in several cases.

On the other hand, with $AlEt_2Cl$, no product was detected.

$Ni(AA)_2$ or $NiCl_2$-$AlEt_3$ or $AlEt_2Cl$ System. The results are summarized in Table 5. The catalyst system immediately became brown-black and homogeneous when either $AlEt_3$ or $AlEt_2Cl$ was added except in the case of $AlEt_2Cl$ ($AlEt_2Cl/Ni(AA)_2=2$), in which it immediately became dark green and homogeneous.

In this system, the I and IV monoolefins and the XI and XII diolefins were formed, with the monoolefins the main products in every case. Therefore, in this system, the metal alkenyls, I_m and IV_m, may be rather stable, as in the case of a titanium or vanadium catalyst.

A very small amount of an oily yellow polymer was formed in several cases.

Even with $AlEt_2Cl$, the I and IV monoolefins were formed at the $AlEt_2Cl/Ni(AA)_2$ molar ratio of 2. This result is different from that in the $Fe(AA)_3$ or the $Co(AA)_2$ catalyst.

The results obtained from the variation in the $AlEt_3/M(AA)_n$ ($M(AA)_n$: $Fe(AA)_3$, $Co(AA)_2$, or $Ni(AA)_2$) molar ratio showed that the amount of metal-ethyl bonds (or metal-hydrogen bonds) reaches a maximum at the molar ratio of a unit. This suggests that, with an increase in the $AlEt_3/M(AA)_n$ molar ratio, the valence state of transition metal is reduced to metal(0) and that the

TABLE 6. SEVERAL TRANSITION-METAL SALT-$AlEt_3$ SYSTEMS[a)]

Transition-metal		Al/MX_n[d)]	Reaction		Products (mol% of MX_n)	
salt	mmol		Temp (°C)	Time(min)	IV	I
$ZrCl_4$[b)]	3.9	1	30	100	1.3	0.9
$ZrCl_4$[b)]	4.0	1	0	100	0.2	0.1
$ZrCl_4$[b)]	3.7	1	−30	150	0	0
$NbCl_5$[c)]	3.4	1	30	60	0.2	0.3
$NbCl_5$[c)]	3.3	1	0	60	0.7	0.6
$Cr(AA)_3$	1.5	2	30	60	0.1	0.1
$CrCl_3$	1.3	2	30	60	0	0.7
$CrCl_2$	1.5	2	30	60	0	0
$Mn(AA)_2$	1.5	2	0	120	0	0

a) The conditions are same as in Table 3
b) Aging temperature: 30°C, Aging time: 1 hr
c) Aging time: 15 min
d) $AlEt_3$/transition-metal salt molar ratio

amount of the metal-ethyl bonds effective for isoprene insertion decreases. The amount of the products in these systems gradually increased over the reaction time of 120 min, as is shown in Tables 3, 4, and 5.

Others. In the $ZrCl_4$-$AlEt_3$ catalyst system, the catalyst mixture remained heterogeneous; the liquid phase was dark brown, and the solid phase, dark orange.

In this system small amounts of monoolefins, I and IV, were formed. Increases in their amounts were observed when the reaction temperature was made higher.

The catalyst mixture became almost homogeneous after it had been aged for *ca.* 2 hr at 50°C, but when isoprene was introduced into the heterogeneous catalyst mixture at 30°C it became homogeneous and brown-red after 20 min. This shows that the state of the catalyst mixture was changed by adding isoprene. No such behavior was observed in the other systems, perhaps indicating the formation of a new complex participated with isoprene, but no further study was made.

In the $NbCl_5$-$AlEt_3$ catalyst system, the catalyst system became brown-black and homogeneous when $AlEt_3$ was added. In this system, small amounts of I and IV were formed.

In the $Cr(AA)_3$-$AlEt_3$ system, the aged mixture became brown-black and homogeneous, but in the $CrCl_3$ or $CrCl_2$-$AlEt_3$ system, the violet solid phase of $CrCl_3$ or $CrCl_2$ itself remained. In the $Cr(AA)_3$-$AlEt_3$ system, the I and IV monoolefins were formed, but they were present in very small amounts. Kapur *et al.*[5] have reported that the maximum activity of the $Cr(AA)_3$-$AlEt_3$ catalyst system in isoprene polymerization is obtained beyond the molar ratio of 4. In view of this, the insertion reaction was also carried out at the molar ratio of 5; the amounts of the monoolefins thereupon increased slightly. In the $CrCl_3$-$AlEt_3$ system, a small amount of I was formed, but in the $CrCl_2$-$AlEt_3$ system, no products were detected.

In the $Mn(AA)_2$-$AlEt_3$ system, the aged mixture became light brown but remained heterogeneous. In this system, no products were detected, either.

In the zirconium and niobium catalysts, a small amount of a sticky polymer was formed, but in the other systems no polymer was formed.

On the other hand, with $AlEt_2Cl$, no products at all were detected in these systems.

The Effects of Additives. The effects of the addition of a Lewis base to the several catalyst systems studied above were also examined. The catalyst mixture was prepared by adding materials in the following order: a transition-metal salt, a base, a solvent (toluene), an internal standard (methylcyclohexane), and an ethylaluminum compound. The state of the aged mixture was almost the same as that without an additive in every case.

Zambelli *et al.*[6] have reported that, in the polymerization of propylene to a syndiotactic polymer, the addition of a Lewis base such as anisole to the VCl_4-$AlEt_2Cl$ catalyst system (anisole/VCl_4 molar ratio = 1—2) makes the catalyst mixture active. The effect of the addition of anisole on the insertion reaction in this catalyst system was examined. The amounts of I and IV increased at the temperature of −70°C, but quite substantially decreased at 0°C. These findings agree with that obtained by Zambelli *et al.*[6]; the catalyst mixture is stable at temperatures lower than −40°C.

Misono *et al.*[7-9] have reported that a stable

Table 7. Effect of additives[a)]

MX_n	Base	Base/MX_n[d)]	Products (mol% of MX_n)							
			XI	IV	VII	VIII	I	XII	IX	X
VCl_4[b)]	anisole	1.0	0	15.4	0	0	1.8	0	0	0
VCl_4[c)]	anisole	1.0	0	1.4	0	0	0.4	0	0	0
$Fe(AA)_3$	PPh_3	1.0	0	1.0	0.4	0.7	0	0	0	0
$Fe(AA)_3$	$P(n\text{-}Bu)_3$	1.0	0	1.2	1.8	2.1	0	0	0	0
$Fe(AA)_3$	dipyridyl	0.5	0	0	26.1	28.2	4.2	0	1.2	0
$Co(AA)_2$	dipyridyl	0.5	0.1	2.5	0.6	0	1.5	0.1	0.6	0.8
$Ni(AA)_2$	dipyridyl	0.5	0.3	1.4	0	0	1.6	0.5	0	0

a) The conditions are same as in Table 3, Reaction temperature: 30°C Reaction time: 120 min
M(AA): 1.5 mmol $AlEt_3$/M(AA) molar ratio: 2.0

b)c) Aging temperature: −70°C Aging time: 5 min VCl_4: 1.0 mmol $AlEt_2Cl/VCl_4$ molar ratio: 3.0

b) Reaction temperature: −70°C Reaction time: 30 min

c) Reaction temperature: 0°C Reaction time: 30 min

d) Base/transition-metal salt molar ratio

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complex with a metal-ethyl bond can be isolated by adding α,α'-dipyridyl to the metal acetylacetonate (metal: Fe, Co, or Ni)-diethylaluminum monoethoxide system. The effects of the addition of α,α'-dipyridyl on the insertion reaction in the Fe-$(AA)_3$, $Co(AA)_2$, or $Ni(AA)_2$-$AlEt_3$ catalyst system were also examined. In the iron catalyst, the amounts of VII and VIII increased markedly and XI were newly formed. This may be explained as follows: a) The amount of iron-ethyl bonds (or iron-hydrogen bonds) is increased by the α,α'-dipyridyl. b) The iron-ethyl bonds are slightly stabilized by the α,α'-dipyridyl and the monoolefin (I) is formed by the methanolysis of the corresponding metal alkenyl (I_m), which is also stabilized. On the other hand, the effects of the addition of α,α'-dipyridyl were not so pronounced for the cobalt or the nickel system. The difference between Fe and Co or Ni is considered to be due partly to the difference in their valence states.

The effects of the addition of PPh_3 or $P(n\text{-}C_4H_9)_3$ to the $Fe(AA)_3$-$AlEt_3$ catalyst system were also examined. In both cases, the amounts of VII and VIII decreased and IV was newly formed. This result indicates that PPh_3 and $P(n\text{-}C_4H_9)_3$ are more strongly coordinated to metal than α,α'-dipyridyl; therefore, it becomes difficult for the insertion reaction itself to occur, but the iron-ethyl bonds are rather stabilized and the monoolefin (IV) is formed.

From the above results, it can be concluded that the stabilities of the metal alkenyls formed by the insertion reaction decrease in the following order: $Ti \cong V \gg Ni > Co > Fe$.