# DIMERIZATION OF ETHYLENE CATALYZED BY $\beta$ -DIKETONATE COMPLEXES OF COBALT AND NICKEL\*

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#### Summary

The M(acac)<sub>n</sub>-R<sub>x</sub> Al<sub>2</sub>Cl<sub>6-x</sub> (M = Co, n = 2 or 3; Ni, n = 2; R = Et, i-Bu) system, both in the presence and absence of additives, is used for the dimerization of ethylene to a mixture of olefins consisting predominantly of 2-butenes. With the  $Co(acac)_3$ -Al(i-Bu)<sub>3</sub> system, a maximum conversion of 76% with selectivity to 2-butenes of 98 is achieved at 25  $^{\circ}$ C and 8 kg cm<sup>-2</sup> ethylene pressure. Selectivity to 2-butenes is higher with the Co(III) complex compared to Co(II) in combination with trialkylaluminum. However, the three-component Co(acac)<sub>2</sub>-Et<sub>2</sub>AlCl-PR<sub>3</sub> system is superior to Co(acac)<sub>3</sub>-Et<sub>2</sub>AlCl-PR<sub>3</sub> for the dimerization of ethylene to 2-butenes. The activity of  $Co(R^1COCHCOR^2)_2$  in combination with alkylaluminum cocatalysts decreases when  $R^1$ ,  $R^2$  in the complex are Ph, Ph > CH<sub>3</sub>, CH<sub>3</sub> > Ph, CH<sub>3</sub> > CF<sub>3</sub>,  $CF_3$  for AlEt<sub>3</sub> and  $CF_3$ ,  $CF_3 > Ph$ , Ph > Ph,  $CH_3 > CH_3$ ,  $CH_3$  for  $Et_3Al_2Cl_3$ . For Ni(acac)<sub>2</sub>-Et<sub>2</sub>AlCl-PR<sub>3</sub>, the selectivity to 2-butenes decreased in the following order for  $PR_3$ :  $P(n-Bu)_3 \approx DIPHOS > PPh_3 > P(OPh)_3$ . The effects of ethylene pressure and reaction temperature on the activity and selectivity to 2-butenes are also investigated.

### Introduction

The dimerization of simple olefins in the presence of homogeneous transition metal catalysts has been extensively studied [1-5]. Various  $\beta$ -diketonate complexes of Group VIII transition metals in different oxidation states in combination with alkylaluminum cocatalysts are used [6-10] for the dimerization and trimerization of ethylene. In such systems it is possible to vary the catalyst composition and thereby study the influence of such modifications on the nature and the distribution of the products.

A systematic study of the dimerization of ethylene catalyzed by soluble titanium alkoxides in conjunction with trialkylaluminum was reported from this laboratory [11]. The major product of dimerization was identified as 1-butene. The main objective of the present investigations has been to optimise conditions for the formation of 2-butenes as major dimerization

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products. In this paper we report the results of our studies on the dimerization of ethylene employing the  $\beta$ -diketonate complexes of cobalt and nickel under comparable conditions in order to correlate the structure of the catalyst with activity and selectivity.

## Experimental

All manipulations involving air-sensitive compounds were performed in a glove-box. Solvents were distilled and dried over sodium before use.

Melting points (uncorrected) were determined on a Toshniwal melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 567 instrument. Metal analysis was conducted by atomic absorption methods on a Varian 1200 instrument. Gas chromatographic analyses were carried out on a Shimadzu GC-7AG gas chromatograph with a  $3 \text{ mm} \times 2 \text{ M}$  column packed with squalene (20%) on Chromosorb W. Retention times for different gaseous products were compared with values for authentic samples. Mass spectra were recorded on a HP-5985 instrument attached to an Electron Capture detector (70 eV).

# Materials

The following chemicals were used as such:  $Co(acac)_2$ ,  $Fe(acac)_3$ . DIPHOS (Alfa Products, U.S.A.), PPh<sub>3</sub> (Aldrich), P(n-Bu)<sub>3</sub>, P(OPh)<sub>3</sub> (Fluka, AG), triethylaluminum, triisobutylaluminum, ethylaluminum sesquichloride (Ethyl Corporation, U.S.A.). Diethylaluminum chloride (supplied by Poly Olefins Industries, Ltd., Thane, India) was used as a 15.5 wt.% solution in benzene or heptane.

 $Ni(acac)_2$  and  $Co(acac)_3$  were prepared as per literature methods [12].

## Bis (1,3-diphenyl-1,3-propanedionato)nickel (II)/cobalt (II) [Ni(dbm)<sub>2</sub>/Co(dbm)<sub>2</sub>]

These complexes were prepared according to the following procedure: A mixture of 5 mmol of the metal acetate in absolute ethanol (30 ml) and 10 mmol of dibenzoylmethane (H-dbm) in 25 ml of the same solvent were refluxed for 3 h. The solution was cooled in ice when the complex separated out. It was filtered, washed carefully with hot alcohol and dried. Complexes were further purified by recrystallization from THF-heptane (1:5 v/v) mixture.

 $\begin{array}{c} Co(dbm)_2 \ [13] \ yellowish \ brown, \ m.p. \ 207-9 \ ^\circ C, \ M^+ \ (505.4), \ IR \\ (KBr, cm^{-1}) \ 1582 \ (C=C), \ 1525 \ (C=O) \ and \ 455 \ (M=O). \ Anal. \ calcd. \ for \\ C_{30}H_{22}O_4Co: \ Co, \ 11.66\%; \ found: \ Co, \ 11.24\%. \end{array}$ 

 $Ni(dbm)_2$  [14] green, m.p. 255 °C(d),  $M^+$  (504.3), IR (KBr, cm^{-1}) 1592 (C=C), 1550 (C=O) and 460 (M=O). Anal. calcd. for  $C_{30}H_{22}O_4Ni$ : 11.62%; found: Ni 11.51%.

 $Bis(1-phenyl-1,3-butanedionatonickel(II)/cobalt(II)[Ni(ba)_2/Co(ba)_2]$ 

These were synthesized using benzoylacetone(Hba) as the ligand in a manner similar to the above, except that the reflux time was reduced to 1 h. Complexes were recrystallized from THF-heptane (1:5 v/v) mixture.

Co(ba)<sub>2</sub> [15] brown, m.p. 118–120 °C, M<sup>+</sup>(381.2), IR (KBr, cm<sup>-1</sup>) 1580 (C=C), 1545 (C=O), 452 (M-O). Anal. calcd. for  $C_{20}H_{18}O_4Co$ : Co, 15.45%; found: Co 15.36%.

Ni(ba)<sub>2</sub> [15] green, m.p. 172–4 °C, M<sup>+</sup>(380.6), IR (KBr, cm<sup>-1</sup>) 1588 (C=C), 1552 (C=O), 461 (M=O). Anal. calcd. for  $C_{20}H_{18}O_4Ni$ : Ni, 15.40%; found: Ni 15.29%.

# Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)nickel(II)/cobalt(II)[Ni(hfac)<sub>2</sub>/Co(hfac)<sub>2</sub>]

1.5 g of the nickel(II) or cobalt(II) acetate was dissolved in about 10 ml of dry methanol. To this was added a solution of hexafluoroacetylacetone (hfac, 1.8 ml in 5 ml methanol). The resulting mixture was warmed on a hot plate with constant stirring. It was further concentrated to a small volume (5 ml). The flask was then chilled in ice when the complex separated. The crude product was filtered, washed with hot methanol and dried. It was recrystallized from absolute alcohol-petroleum benzene (40-60 °C) mixture (1:20 v/v).

 $Co(hfac)_2$ , reddish brown, mp. 153 °C(d), M<sup>+</sup> (473.0). Anal. calcd. for  $C_{10}H_2O_4F_6Co$ : Co, 12.45%; found: Co 12.30%.

Ni(hfac)<sub>2</sub> green, m.p. 205 °C,  $M^+$  (472.0). Anal. calcd. for  $C_{10}H_2O_4F_6N_i$ : Ni, 12.42%; found, Ni 12.21%.

The IR spectra of these complexes are in agreement with the values reported in the literature [16].

# A representative procedure for the dimerization of ethylene at atmospheric pressure

In a 250 ml three-necked flask equipped with a thermometer port, an inlet tube for introducing ethylene, and a condenser connected to a calibrated gas burette was placed 70 ml of dry toluene. The solvent was stirred and the temperature maintained at  $25 \pm 1$  °C. After the system was thoroughly flushed with argon for ~5 min, ethylene was fed into the reactor until the solvent was saturated (~1 h). The burette was then filled with ethylene under atmospheric pressure. The catalyst (metal  $\beta$ -diketonate 2 mmol) in 9 ml toluene and 1.09 ml of Et<sub>3</sub>Al were injected into the reactor. The ethylene absorption commenced immediately and was followed using the manometer. The reaction was terminated by injecting 2 ml of n-butanol after 60 min. During the course of the reaction, both gas and liquid samples were withdrawn at regular intervals of time and analyzed by GC.

#### Dimerization at higher pressures

In a typical experiment, 400 ml of dry toluene (previously saturated with ethylene) was introduced into a 600 ml two-necked addition funnel. 4 mmol of the transition metal  $\beta$ -diketonate, 28 mmol of the alkylaluminum and 12 mmol of the phosphine were added to the solvent. The above catalyst

solution was carefully charged into a 2-litre Parr reactor. Ethylene was then introduced into the reactor until the required pressure was attained and then agitation was begun. The reaction was terminated after 30 min and the volume of gaseous reaction products were measured using a calibrated aspirator bottle. The products were further analysed as before [11].

#### **Results and discussion**

## $Co(acac)_3$ -AlR<sub>3</sub>/AlR<sub>x</sub>Cl<sub>3-x</sub> system

The dimerization of ethylene catalyzed by  $Co(acac)_3-AlR_3$  (R = Et; i-Bu) at atmospheric pressure is shown in Fig. 1. Higher ethylene conversion and poor selectivity to 2-butenes is observed with  $Al(i-Bu)_3$  compared to  $AlEt_3$ . However, selectivity to 2-butenes is higher with  $AlEt_3$ . Another feature of this system is that the weight percentage of hexenes among the products is in the range of 8-15%.

A maximum ethylene conversion of 76% is observed with  $Co(acac)_3$ -Al(i-Bu)<sub>3</sub> at 8 kg cm<sup>-2</sup> ethylene pressure (Table 1). The product mixture consists predominantly of 2-butenes. Addition of an electron donor, PPh<sub>3</sub>, suppresses the dimerization reaction considerably. With AlEt<sub>3</sub> good selectivity to 2-butenes is observed at high pressures (runs 3 and 4). Increasing the



Fig. 1. Dimerization of ethylene catalyzed by  $Co(acac)_3$ -AlR<sub>3</sub> system at 25 °C; ( $\odot$ ) R = i-Bu, ( $\Box$ ) R = Et; ( $\triangle$ ) 1-Butene, ( $\Box$ ) 2-Butenes.

#### TABLE 1

Run	Cocatalyst (II)	Additive (III)	Ratio of I:II:III (mol)	Temp.	Pressure (kg cm <sup>-2</sup> )	Conv. (wt.%)	Selectivity <sup>c</sup>		
				(°C)			<u>1—В</u>	2В	Н
1	Al(i-Bu) <sub>3</sub>	_	1:4	25	8	75.8	1.5	97.9	0.6
2	$Al(i-Bu)_3$	PPh <sub>3</sub>	1:4:1	25	8	1.6	92.7	7.1	
3	AlEt <sub>3</sub>	_	1:4	25	8	71.8	22.0	78.0	
4	AlEt <sub>3</sub>	_	1:4	25	6.8	74.5	19.3	80.6	_
5	AlEta	_	1:4	25	1	<b>59.0</b>	22.3	69.4	8.3
6	AlEt <sub>3</sub>	_	1:5	25	8	66.2	18.2	80.8	0.9
7	AlEt <sub>3</sub>	_	1:4	55	8	72.4	11.8	88.2	
8 <sup>b</sup>	Et <sub>2</sub> AlCl	_	1:4	25	8	0.7	71.3	28.7	
9 <sup>b</sup>	Et <sub>2</sub> AlCl	PPh <sub>3</sub>	1:7:3	50	8	0.5	100		
10	$Et_3Al_2Cl_3$	$PPh_3$	1:7:3	50	8	0.0	—		_

Dimerization of ethylene with Co(acac)<sub>3</sub> (I)-cocatalyst system<sup>a</sup>

<sup>a</sup>Reaction conditions: 30 min, toluene (500 ml).

<sup>b</sup>15% (w/w) Et<sub>2</sub>AlCl in benzene was used.

<sup>c</sup>Selectivity =  $\frac{\text{weight of A}}{\text{weight of } (A + B + C)} \times 100$ ; 1-B = 1-butene; 2-B = 2-butenes; H = hexenes.

molar ratio of cocatalyst/catalyst (run 6) decreases the conversion slightly and the product fraction contains <1% of hexenes. When the reaction is carried out at higher temperature, (55 °C) the isomerization of 1-butene to 2-butenes becomes significant. The activity of Co(III) complex with Et<sub>2</sub>AlCl is poor (<1% conversion, runs 8 and 9).

Acetylacetonates of Fe(III), VO(IV) and Mo(VI) in combination with various alkylaluminum cocatalysts have shown no potential for the dimerization of ethylene under similar conditions.

## $Co(acac)_2 - AlR_3 / AlR_x Cl_{3-x}$ system

The reactivity and selectivity of  $Co(acac)_2$  in combination with various alkylaluminum cocatalysts for dimerization of ethylene to 2-butenes is shown in Table 2. Use of  $AlEt_3$  as cocatalyst gives poor selectivity to 2-butenes under the above conditions. However, the  $Co(acac)_3$ -AlEt<sub>3</sub> system (Table 1, run 3) is a superior catalyst from the point of view of ethylene conversion and selectivity to 2-butenes. The role of THF is manifold. It dissolves the Co(II) complex completely and electronically modifies the cobalt metal centre through the coordination of the lone pair of electrons on the oxygen atom. The labile THF may be responsible for the high activity of the Co(II) complex system in comparison to THF-free system. Jordan and coworkers [17, 18] have demonstrated that  $CP_2Zr(R)(THF)^+$  (R = CH<sub>3</sub>, H, Ph, etc.) are good polymerization catalysts for ethylene, and one of the reasons for the high activity of the system is attributed to the lability of THF. With Al(i-Bu)<sub>3</sub> cocatalyst, the reaction is sluggish (run 3) possibly due to the steric influence of coordinated THF on the isobutyl group. The cobalt(II)-aluminum alkyl system generally exhibits a proportional increase in selectivity to 2-butenes

Run	Cocatalyst	Additive (III)	Ratio of I:II:III <sup>b</sup> (mol)	Temp. (°C)	Conv. (wt.%)	Selectivity		trans-2-B	
	(11)					1-B	2-B	cis-2-B	
1	AlEt <sub>3</sub>		1:4	25	21.8	86.5	13.5	5.1	
2	AlEt <sub>3</sub>	THF	1:4:30	25	56.0	33.0	67.0	3.9	
3	Al(i-Bu) <sub>3</sub>	THF	1:4:30	25	27.7	71.4	28.6	3.9	
4 <sup>c</sup>	Et <sub>2</sub> AlCl	PPh <sub>3</sub>	1:7:3	50	92.8	2.7	97.3		
5°	Et <sub>2</sub> AlCl	$P(OPh)_3$	1:7:3	50	24.2	24.5	75.5	1.01	
6°	<b>Et</b> <sub>2</sub> AlCl	DIPHOŠ	1:7:3	50	1.0	100		_	
7°	Et <sub>2</sub> AlCl	$P(n-Bu)_3$	1:7:3	50	0.0	_	_		
8	$\tilde{\mathbf{Et_{3}Al_{2}Cl_{3}}}$	PPh <sub>3</sub>	1:7:3	55	15.4	84.0	15.9	1.9	

Dimerization of ethylene in the presence of  $Co(acac)_2$  (I)-AlR<sub>3</sub><sup>a</sup>

<sup>a</sup>Reaction conditions: 30 min;  $P(C_2H_4) = 8 \text{ kg cm}^{-2}$ ; toluene (500 ml).

<sup>b</sup>Sequence of mixing: 1–III–II.

°15% (w/w) Et<sub>2</sub>AlCl in benzene was used.

as the ethylene conversion increases. Formation of hexenes is also, not observed under the experimental conditions used in these studies. The formation of 1-butene and 2-butenes during the course of the catalytic process is of interest [19, 20]. In general, the equilibria among the butenes under ethylene dimerization conditions can be represented as in Fig. 2.

The thermodynamic equilibrium concentrations of butenes at 26 °C, (in mol%) are 1-butene, 3; *cis*-2-butene, 22; and *trans*-2-butene 75, respectively [21,22]. However, the compositions of butenes (Table 2) obtained with  $Co(acac)_2$ -AlR<sub>3</sub> systems are different. This difference may be attributed to the fact that thermodynamic equilibrium is not attained in the system, since the isomerization of 1-butene to 2-butenes is a secondary reaction during ethylene dimerization. The isomerization becomes insignificant at higher ethylene concentration (pressure) in the liquid phase [22].

The three-component catalyst system  $Co(acac)_2-Pr_3-Et_2AlCl$  shows decreasing activity with decreasing  $\pi$ -acceptor strength of the tertiary phosphine used. With PPh<sub>3</sub>, the thermodynamic equilibrium concentration of butenes is attained. The  $Co(acac)_3-Et_2AlCl-P(n-Bu)_3$  system does not show any activity for dimerization of ethylene. It is probable that Co(III) is not



Fig. 2. Equilibria between ethylene and butenes.

TABLE 2

Run	$\mathbb{R}^1$	R <sup>2</sup>	Cocatalyst (II)	Ratio of I:II (mol)	Conv. (wt.%)	Selectivity		trans-2-B
						1-B	2-B	cis-2-B
1	CH <sub>3</sub>	CH <sub>3</sub>	AlEt <sub>3</sub>	1:4	56	33	67	3.9
2	Ph	CH <sub>3</sub>	AlEt <sub>3</sub>	1:4	46	46.4	<b>53.6</b>	3.6
3	Ph	Ph	AlEt <sub>3</sub>	1:4	74.3	17.0	83.0	3.4
4	CF <sub>3</sub>	CF <sub>3</sub>	AlEt <sub>3</sub>	1:4	0.0	_	_	_
5	CH <sub>3</sub>	CH <sub>3</sub>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1:30	17.2	55.1	44.9	1.5
6	Ph	CH <sub>3</sub>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1:30	30.8	45.4	54.5	0.9
7	Ph	Ph	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1:30	21.7	56.3	43.7	
8	$CF_3$	$CF_3$	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1:30	56.3	31.9	68.1	2.3

TABLE 3 Effect of  $\beta$ -diketone of Co(R<sup>1</sup>COCHCOR<sup>2</sup>)<sub>2</sub> (I) on the dimerization of ethylene<sup>a</sup>

<sup>a</sup>Reaction conditions:  $28 \pm 1$  °C;  $p(C_2H_4) = 8 \text{ kg cm}^{-2}$ ; Co(II):THF (mol) = 1:30; toluene (475 ml).

reduced to the same extent as Co(II) in generating the catalytically active species. When  $Et_2AlCl$  is replaced by  $Et_3Al_2Cl_3$ , the catalytic efficiency of the system with Co(II) complex is decreased due to the lower reducing power of the latter.

The influence of substituents in  $\beta$ -diketone ligand coordinated to Co(II) ion on the dimerization of ethylene is shown in Table 3. The  $\beta$ -ketoenolate ions form very stable chelate compounds with a wide variety of metal ions, including Co(II), Co(III) and Ni(II) [23, 24].



The complex (1) in combination with the Lewis acid AlEt<sub>3</sub> forms the catalytically active species with cobalt ion in different oxidation states (eqn. 1);

$$\begin{array}{ccc} \text{Co}^{\text{II}} + \text{AlR}_3 & \xrightarrow{\text{THF}} & \text{Co}^{\text{I}} + \text{Co}^{0} \\ & & & \downarrow \\ & & \text{AlR}_3 & \text{Cobalt slurry} \end{array}$$
(1)

Mitsudo and coworkers [25] have reported the formation of similar reduced cobalt species with LiAlH<sub>4</sub> in THF for the hydrogenation of carbon monoxide to olefins. As the electrophilicity of the cobalt metal center in the complex  $Co(R^1COCHCOR^2)_2$  decreases (in the following order, when  $R^1$  and  $R^2$  are  $CF_3$ ,  $CF_3 > Ph$ ,  $CH_3 > CH_3$ ), over-reduction of the metal may be possible. This results in poor activity of the cobalt complex with hexafluorosubstituted acetylacetonates. On the other hand, the presence of two phenyl substituents on the  $\beta$ -diketone ligand can exert a certain steric influence on the geometry of the complex 1, leading to distortions of the configuration and subsequently favouring the generation of catalytically active species.

The activity of substituted cobalt(II) acetylacetonates with  $Et_3Al_2Cl_3$  cocatalyst for the dimerization of ethylene decreases when  $R^1$  and  $R^2$  in  $Co(R^1 COCHCOR^2)_2$  follows the order:

 $CF_3, CF_3 > Ph, CH_3 > CH_3, CH_3.$ 

The above trend is almost the reverse of the activity observed with  $AlEt_3$  cocatalyst. The Lewis acidity and reducing nature of the ethylaluminum sesquichloride are lesser than that of  $AlEt_3$ , thereby stabilizing the active species generated in the liquid phase. Diphenyl-substituted  $\beta$ -diketone ligated to Co(II) complex as with the Co(II)-AlEt<sub>3</sub> system exerts a certain amount of steric influence during the dimerization of ethylene.

### $Ni(acac)_2 - AlR_3 / AlR_x Cl_{3-x}$ system

The dimerization of ethylene to butenes catalyzed by Ni(II)  $\beta$ diketonates in combination with different cocatalysts and additives was studied (Table 4). Good conversion and selectivity to 2-butenes are achieved with the three-component Ni(acac)<sub>2</sub>-Et<sub>2</sub>AlCl-PPh<sub>3</sub> system along with byproduct hexenes (~6%). As in the case of Co(II) ion, Ni(CF<sub>3</sub>COCHCOCF<sub>3</sub>)<sub>2</sub> in combination with Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> is more active than Ni(acac)<sub>2</sub>. The 2butenes/1-butene ratio corresponds to that of the thermodynamic equilibrium concentration. However, the *trans*-2-butene/*cis*-2-butene ratio is below the equilibrium value, suggesting that the routes A and B of Fig. 2 are

TABLE 4

Activity of  $Ni(R^1COCHCOR^2)_2$  (I) for dimerization of ethylene under different conditions<sup>a</sup>

Run	<b>R</b> <sup>1</sup> , <b>R</b> <sup>2</sup>	Cocatalyst (II)	Additive (III)	Ratio of I:II:III (mol)	Temp. (°C)	Conv. (wt.%)	Selectivity			trans-2-B	
							1-B	2-B	н	cis-2-B	
1	CH <sub>3</sub> , CH <sub>3</sub>	AlEta	_	1:4	25	1.7	81.4	18.6			
2	CH <sub>3</sub> , CH <sub>3</sub>	AlEta	THF	1:4:30	25	5.0	20.8	79.2	_	13.5	
3 <sup>b</sup>	CH <sub>3</sub> , CH <sub>3</sub>	Et <sub>2</sub> AlCl	_	1:4	25	9.8	53.3	41.3	5.4	1.4	
4	CH <sub>3</sub> , CH <sub>3</sub>	Et <sub>2</sub> AlCl	THF	1:4:30	25	0.1	<b>46</b> .2	53.8	_	1.33	
5	CH <sub>3</sub> , CH <sub>3</sub>	Et <sub>2</sub> AlCl		1:7	55	—	_	—	_	_	
6	CH <sub>3</sub> , CH <sub>3</sub>	Et <sub>2</sub> AlCl	PPh <sub>3</sub>	1:4:1	25	4.0	68.2	31.8		1.72	
7	CH <sub>a</sub> , CH <sub>a</sub>	Et_AlCl	PPh <sub>3</sub>	1:7:3	25	95.4	0.3	93.8	5.9		
8	Ph, Ph	AlĒta	THF	1:4:30	25	2.4	36.6	63.6	—	2.11	
9	CH <sub>3</sub> , CH <sub>3</sub>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	THF	1:30:30	25	48.5	6.2	93.8	_	2.5	
10	CF <sub>3</sub> , CF <sub>3</sub>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	THF	1:30:30	25	66.2	2.8	97.2	—	2.7	

<sup>a</sup>Reaction conditions:  $p(C_2H_4) = 8 \text{ kg cm}^{-2}$ ; 30 min.

<sup>b</sup>15% (w/w) Et<sub>2</sub>AlCl in benzene was used.

 ${}^{c}p(C_{2}H_{4}) = 9.3 \text{ kg cm}^{-2}.$ 

faster than route C for this system. A similar preference has been observed with the Ni(acac)<sub>2</sub>-Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> system, wherein the 2-butenes/1-butene ratio approaches the equilibrium value with a further decrease in the *trans*-2 butene/*cis*-2-butene ratio. The above results are in agreement with the basic features of isomerization of terminal olefins to internal olefins [26, 27].

The influence of different phosphine additives on conversion and selectivity in the dimerization of ethylene catalyzed by the  $Ni(acac)_2$ -Et<sub>2</sub>AlCl system is shown in Table 5. It is clear from the data that the effect of additives on conversion follows the order:

 $P(n-Bu)_3 > DIPHOS \approx PPh_3 > P(OPh)_3$ 

This is in accordance with the decreasing basicity of the tertiary phosphine/phosphite ligands.

In the oligomerization of olefins catalyzed by nickel complexes, the active catalytic species is postulated to contain the Ni—H bond [29, 30]. In propylene dimerization catalyzed by  $Ni(acac)_2-Et_3Al_2Cl_3-PR_3$  [31], one of the possible configurations proposed for the catalytically active nickel hydride complex is a square planar geometry (2) with tertiary phosphine ligand *trans* to the hydride ligand.



Similar species may be present in this system, influencing the dimerization of ethylene to 1-butene and subsequent isomerization to 2-butenes. There is no correlation between the steric influence exerted by the phosphine ligand (as seen from the cone angle) and the ethylene conversion, proving that the influence of these ligands is only electronic in nature (Fig. 3). In our earlier studies with  $Ti(n-C_4H_9O)_4$ -AlR<sub>3</sub> system [11] it was observed that the facility of formation of 1-butene in presence of the additives followed the trend  $P(OPh)_3 > PPh_3 > P(n-Bu)_3$ . This indicates that the  $\pi$ -acceptor phosphines favour 1-butene compared to  $\pi$ -donor additives.

The pressure dependence of the dimerization of ethylene was studied with Ni(acac)<sub>2</sub>-Et<sub>2</sub>AlCl-PPh<sub>3</sub> in heptane-toluene medium (Fig. 4). At  $3 \text{ kg cm}^{-2}$  ethylene pressure, around 80% conversion was achieved and above  $6 \text{ kg cm}^{-2}$  pressure the increase in conversion was marginal. The maximum selectivity to 2-butenes was 95% at low pressures, whereas the value was >90% at other pressures of ethylene.

The dimerization of ethylene catalyzed by the Ni(acac)<sub>2</sub>-Et<sub>2</sub>AlCl-PPh<sub>3</sub> system is sensitive to the reaction temperature (Fig. 5). As the solubility of ethylene is controlled by the temperature, it has been observed that the conversion of ethylene decreases with increasing temperature. At elevated temperature,  $\beta$ -hydrogen abstraction from  $6 \rightarrow 7$  and subsequently to 5 is

Run	Additive	Conversion (wt.%)	Minimum cone angle (deg)	Selecti	trans-2-B		
	(111)			1-B	2-B	Н	cis-2-B
1	P(n-Bu) <sub>3</sub>	95.3	132 <sup>b</sup>	2.5	90.4	7.2	
2	DIPHOS	83.8	$125\pm2^{\circ}$	3.8	89.9	6.3	
3	PPh <sub>3</sub>	83.7	148 <sup>b</sup>	20.3	77.2	2.5	1.43
4	P(OPh) <sub>3</sub>	35.7	130 <sup>b</sup>	23.9	76.1	<u> </u>	1.3

Effect of phosphine additives on dimerization of ethylene catalyzed by  $Ni(acac)_2$  (I)-Et<sub>2</sub>AlCl (II)<sup>a</sup>

\*Reaction conditions:  $50 \pm 1$  °C;  $p(C_2H_4) = 8 \text{ kg cm}^{-2}$ ; Ni $(acac)_2$ :additive:Et<sub>2</sub>AlCl = 1:3:7; 30 min. <sup>b</sup>See [8].

°Calculated according to [28].

facile in the presence of ethylene (Fig. 6). On the other hand, at low temperature the insertion of 1-butene into the Ni—H bond through  $Ni\rightarrow C_2$  type [5] to give 8 [32] or 9 [33] is facile, leading to 2-butenes and similarly hexenes from 6. Migratory insertion through 10 is insignificant because the presence of tertiary phosphine/phosphite on nickel favours 7 and at high



Fig. 3. Correlation of Tolman electronic factor vs. conversion of ethylene  $(\odot)$ ; selectivity to 1-butene  $(\triangle)$ ; 2-butenes  $(\Box)$ ; hexenes  $(\blacktriangle)$  and 2-butenes/1-butene.

TABLE 5



Fig. 4. Influence of ethylene pressure on conversion  $(\odot)$ , selectivity to 1-butene  $(\boxdot)$ , 2-butenes  $(\blacksquare)$ , hexenes  $(\triangle)$  and *trans*-2-butene/*cis*-2-butene  $(\blacktriangle)$ .



Fig. 5. Effect of temperature on conversion of ethylene ( $\bigcirc$ ), selectivity to 1-butene ( $\boxdot$ ), 2-butenes ( $\triangle$ ), Hexenes ( $\triangle$ ) and 2-butenes/1-butene ratio ( $\blacksquare$ ).





Fig. 6. Dimerization of ethylene and subsequent isomerization catalyzed by the  $Ni(acac)_2 - Et_2AlCl-PPh_3$  system.

concentration of dimerization product, 1-butene, the isomerization by addition and elimination of hydride centres predominates compared to the migratory isomerization of 6 [34].

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