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Dimerization of Ethylene and Propylene Catalyzed by Transition-Metal Complexes†

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Contents

I. Introduction

The dimerization of alkenes is an important method for the production of higher olefins which find extensive application as industrial intermediates. In addition, these reactions serve as good model systems for the study of the reactivity and characterization of metal–carbon bonds. The stimulus in this direction was provided by the pioneering studies of Ziegler in the early 1950s. He explored the use of organoaluminum compounds in the selective dimerization of alkenes. Ever since, workers[1-10,56] in this area have investigated many novel catalytic systems based on transition-metal complexes. In this present review a comprehensive study of the dimerization of ethylene and propylene by transition-metal complexes has been attempted. The literature up to December 1984 is covered. However, dimerization reactions catalyzed by alkali-metal salts are excluded from the present discussions.

II. Mechanisms

Three types of mechanisms are reported[6] for the dimerization of olefins.

A. Degenerated Polymerization

The three important steps involved in this mechanism are (1) initiation reaction (formation of an activated complex), (2) insertion of a monomer into the activated complex, and (3) transfer reaction (deactivation of chain).

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† In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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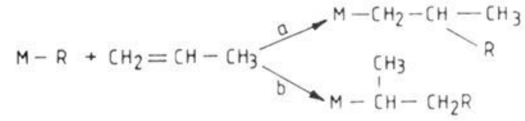
Coordination of the olefin at the metal hydride center and subsequent insertion of the carbon–carbon double bond of the coordinated olefin into the metal–hydride bond can be related to the initial step of a classical polymerization. The metal–carbon bond, formed in this way, inserts a second monomer molecule previously coordinated into the same metal center (the propagation step). The dimer is formed by a β-hydride abstraction, a common cleavage reaction of transition-metal–carbon bonds.[11] The β-hydrogen of the alkyl group attached to the metal is transferred to the latter with formation of the metal hydride, and the organic residue leaves the metal center as a vinylic olefin.[12] The ease of β-hydrogen abstraction depends on the metal, its valency state, and the ligand environment. The metals on the extreme end of the transition series are prone to β-hydrogen abstraction easily from an attached alkyl group. The complexes based on these metals are good catalysts for the dimerization of olefins.

Selectivity to dimerization is related to the ratio of the rate of β-elimination to the rate of insertion or in other words, to the ratio of the rate of chain transfer to the rate of propagation. The temperature does not seem to influence the ratio. Steric course of insertion is sometimes ambiguous. The factors that are vital in deciding the products are not clearly understood. Metal–hydrogen and metal–carbon bonds react with olefins either like hydride ions and carbanions or like protons and carbonium ions (eq 1). The factors influencing the a/b ratio are yet to be ascertained. It may depend on the nature of olefins, the complex involved, and the temperature.

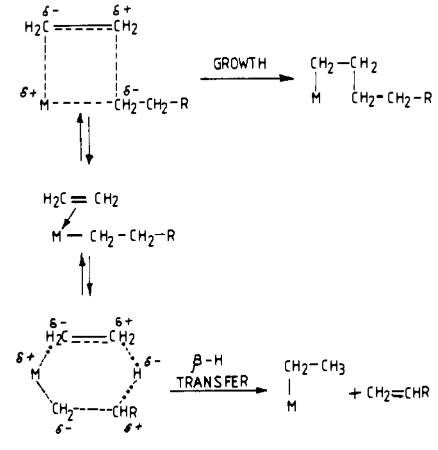


$$M-R + CH_2{=}CH-CH_3 \begin{cases} \xrightarrow{a} M-CH_2-CH(R)-CH_3 \\ \xrightarrow{b} M-CH(CH_3)-CH_2R \end{cases} \quad (1)$$

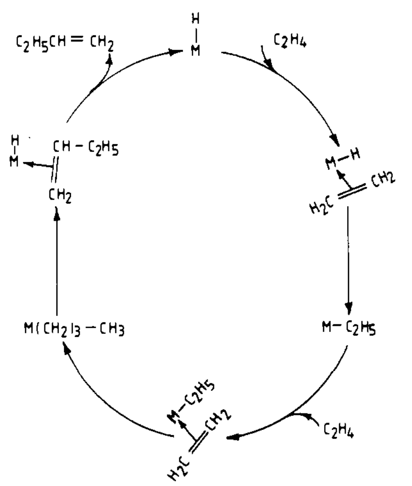
(R = H or ALKYL)

The influence of the ligand on the strength of metal–carbon bond and on the course of the reaction is well explained by Olive and Olive.[13] It is known that the growth step starting from a configuration in which a monomer is coordinated to a transition metal proceeds via a polar, four-center transition state. There is kinetic evidence that both chain growth and β-hydrogen transfer reactions start from the same configuration.[12] A polar, six-centered transition state including a monomer, α-carbon, β-carbon, and one β-H of the growing chain attached to the same metal center leading to β-hydrogen abstraction is suggested. This is supported by ligand effect. Electron-withdrawing ligands withdraw electron density from the metal, thus increasing the positive charge. This polarizes the adjacent bonds including the β-hydrogen, enabling the inclusion of the β-hydrogen into the polar, six-centered transition state (Scheme I). Donor ligands, on the other hand, reduce the positive charge on the metal. Polarization of the adjacent bond is less intensive and hence reaches only

SCHEME I. Chain Growth and β-Hydrogen Transfer from a Metal Alkyl Olefin Complex



SCHEME II. Catalytic Cycle Based on the β-Hydrogen Transfer Route (M = Ni, Rh)

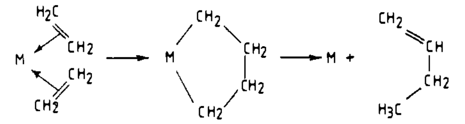


the α-carbon, thus favoring the four-centered transition state. Hence the chain growth is favored. Therefore the ligands can control the nature of reactions.

The catalytic cycle for the dimerization of ethylene based on this mechanism is depicted in Scheme II.[14]

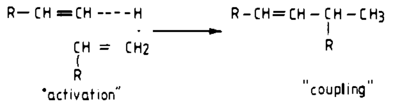
B. Concerted Coupling

This proceeds by the stepwise addition of monomers to the metal followed by the formation of carbon–carbon bonds in a multicentered bond process (eq 2). In



(2)

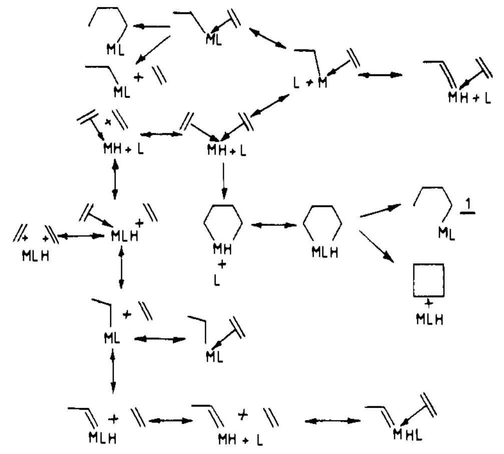
the case of monoolefins it has been formally represented as an activation of the hydrogen–carbon bond followed by coupling (eq 3). In a subsequent proposal the hy-



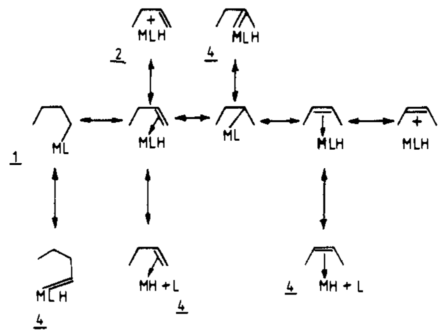
$$\begin{array}{c}\mathrm{R{-}CH{=}CH{\cdots}H}\\ \mathrm{CH{=}CH_2}\\ |\\ \mathrm{R}\\ \text{"activation"}\end{array} \longrightarrow \begin{array}{c}\mathrm{R{-}CH{=}CH{-}CH{-}CH_3}\\ |\\ \mathrm{R}\\ \text{"coupling"}\end{array} \qquad (3)$$

drogen abstraction is represented as an oxidative addition on the metal followed by a reductive elimination and then coupling of the attached elements on a coordinated monomer.[15] The catalysts that follow this route

SCHEME III. Computer-Derived Pathway Starting with MLH and Two Ethylene Molecules



SCHEME IV. Computer-Derived Pathway Starting from Metal Alkyl Complex 1

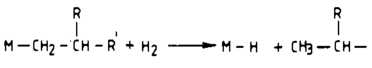


have generally no isomerizing activity and exhibit high selectivity to the dimer product.

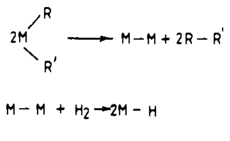
C. Reductive Dimerization

Hydrogen pressure or presence of hydrogen donors or reducing agents can facilitate the dimerization reaction. The products formed are dihydro dimers.

The following hypotheses have been suggested for the mechanisms of these reactions. (1) Hydrogen may act as a chain-transfer agent by hydrogenolysis of the metal–carbon bond when β-elimination is not favored (eq 4). (2) Hydrogen may generate or regenerate a



$$\mathrm{M{-}CH_2{-}\overset{\overset{\displaystyle R}{|}}{C}H{-}R' + H_2 \longrightarrow M{-}H + CH_3{-}\overset{\overset{\displaystyle R}{|}}{C}H{-}R'} \qquad (4)$$



$$2\mathrm{M}{<}^{\mathrm{R}}_{\mathrm{R'}} \longrightarrow \mathrm{M{-}M + 2R{-}R'}$$

$$\mathrm{M{-}M + H_2 \longrightarrow 2M{-}H} \qquad (5)$$

hydride after coupling of two alkyl groups (eq 5). The insertion steps of olefins into metal–hydrogen or metal–carbon bonds are of the same type as depicted in the preceding mechanisms.

Computer-derived pathways for the formation of butenes from the dimerization of ethylene using various organometallic systems are shown in Schemes III and IV.[16] **2** and **3** show the formation of free butenes whereas **4** indicates the computer did not find the formation of free olefins.

III. Catalytic Dimerization of Ethylene Using Transition-Metal Complexes

A large number of dimerization catalysts for alkenes, differing in the composition of the products and in the reaction conditions, have been described.[3] Many papers[17-31] on the mechanism of this reaction under the influence of the homogeneous and gel-immobilized catalysts[32] have appeared.

Among the group Ia elements the alkali-metal compounds like Na_2O, K_2CO_3, and Na_2CO_3 are very versatile dimerization catalysts. Many industrial processes are available on the basis of these catalysts.

A. Group 11 (IB) Elements

There are two reports[33,34] on the dimerization (up to 100%) of ethylene in the presence of a catalyst consisting of Et_2AlCl or $EtAlCl_2$ and $CuAlCl_4$ or Cu_2Cl_2 or $AgAlCl_4$. These catalysts have higher activities at moderate temperatures and pressures compared with those of Friedel–Crafts catalysts.

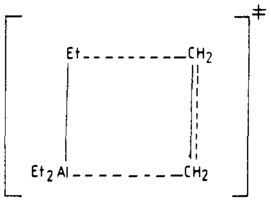
B. Group 12 (IIB) Elements

The only known catalyst for the dimerization of ethylene from this group of elements is $ZnAl_2Cl_8$.[33,34] The cocatalysts employed are Et_2AlCl and $EtAlCl_2$.

C. Group 13 (IIIA) Elements

Aluminum alkyls and related aluminum compounds are well-known catalysts for the dimerization of ethylene. The catalytic potential is a consequence of the readiness with which a trivalent aluminum atom forms electron-deficient or so-called "half" bonds. The kinetics of the homogeneous dimerization of ethylene into 1-butene catalyzed by triethylaluminum in the gas phase has been studied in Teflon-coated reactors at temperatures ranging between 160 and 230 °C.[35] The catalyst is recovered quantitatively from the product mixture. The homogeneous reaction mechanism is summarized in eq 6. The rate-controlling step is the addition of ethylene to $AlEt_3$ to form n-butyldiethylaluminum. The detailed mechanism involves the establishment of a preequilibrium between $AlEt_3$ and ethylene to form a $AlEt_3 \cdot C_2H_4$ complex prior to the formation of the four-center cyclic transition state **5**.[36-38]

$$\begin{aligned}
&[AlEt_3]_2 \rightleftharpoons 2AlEt_3 \\
&AlEt_3 + C_2H_4 \rightleftharpoons Et_2Al(Bu^n) \\
&Et_2AlBu^n \rightleftharpoons Et_2AlH \cdot \text{1-Butene} \\
&Et_2AlH \cdot C_2H_4 \rightleftharpoons AlEt_3
\end{aligned} \qquad (6)$$



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The observed Arrhenius factor of ~$10^{6.2}$ L·mol^{-1} s^{-1} is consistent with a molecule–molecule interaction. Moreover, this low value shows that the formation of a loose π-complex cannot be rate determining but the subsequent step leading to formation of a polar, four-centered transition state becomes rate controlling. Formation of the π-complex is substantiated by IR and NMR observations.

It is claimed that very high yields of pure 1-butene are obtained at low conversions of ethylene.[39-42] Thus it is possible to dimerize ethylene to 1-butene to the extent of 10% and use the resulting mixture for the production of LLDPE copolymer.[41] At higher conversions of ethylene (>20%) appreciable amounts of C_6 and C_8 alkenes are produced along with 1-butene.[43]

D. Group 14 (IVA) Elements

$PbAl_2Cl_8$ with Et_2AlCl or $EtAlCl_2$ is reported as a catalyst for the dimerization of ethylene.[33,34]

E. Group 4 (IVB) Elements

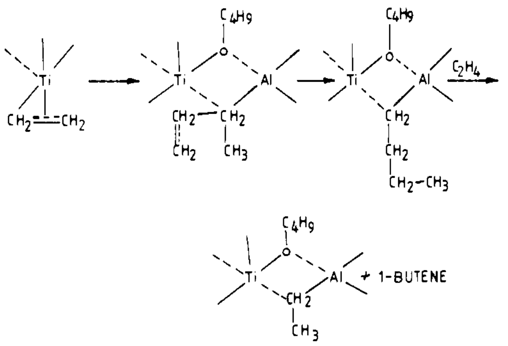
1. Titanium

Titanium compounds, especially halides in conjunction with aluminum compounds known to be good catalysts for polymerization of ethylene, give dimers by minor changes in the constituents of the catalytic mixture or experimental conditions. A mixture of titanium esters and trialkylaluminum produces 1-butene from ethylene.[44]

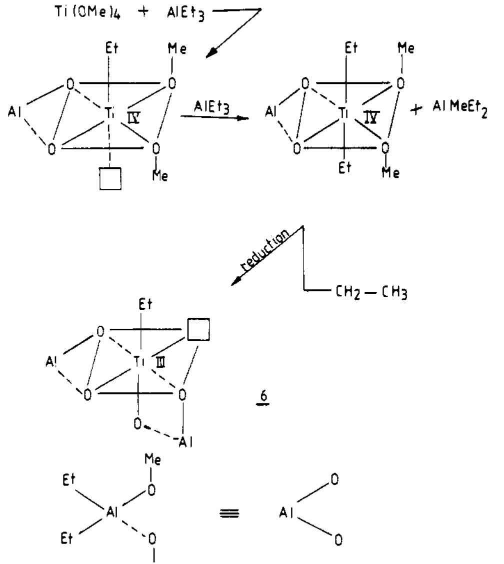
Zhukov and co-workers[45] have reported optimum conditions for the dimerization of ethylene using titanium alkoxides. Ethylene was dissolved under 2.75 atm pressure in heptane containing 5 g/L of $Ti(O\text{-}n\text{-}Bu)_4$ and 20 g/L of $AlEt_3$ and kept for 6–8 h at 60 °C. The resulting solution yielded 99.5% pure 1-butene. A copolymer of 1-butene with ethylene was also formed during this method. Another report[46] claims that the dimerization of ethylene is favored with a ratio of $AlR_3/Ti(OR)_4 < 10$. The dimerization selectivity is high (90%); a major part of the dimers formed is 1-butene with a small amount of 2-butenes. This means that the catalyst system is not a very isomerizing one, and it behaves like triethylaluminum alone, except for the fact that the experimental conditions are much less severe. The physicochemical aspects of the catalyst system have been investigated in detail.[47-53]

Belov and his group[54] have observed the formation of polymers at high pressures of ethylene with titanium alkoxide–trialkylaluminum systems. Operation at low temperatures (ranging from 10 to 40 °C) increases the activity. However, this involves difficulties regarding the problem of heat removal. Use of low-boiling solvents like ethyl chloride and diethyl ether are preferable because they facilitate heat removal, isolation of 1-butene, and rectification of the solvent. Modifiers like organic esters of orthophosphoric acid, diphenylamine, and phenothiazine have been used. The inclusion of these compounds in amounts of 0.1–1 mol/mol of alkylaluminum leads to certain reduction in polymer formation associated with certain loss of activity of the

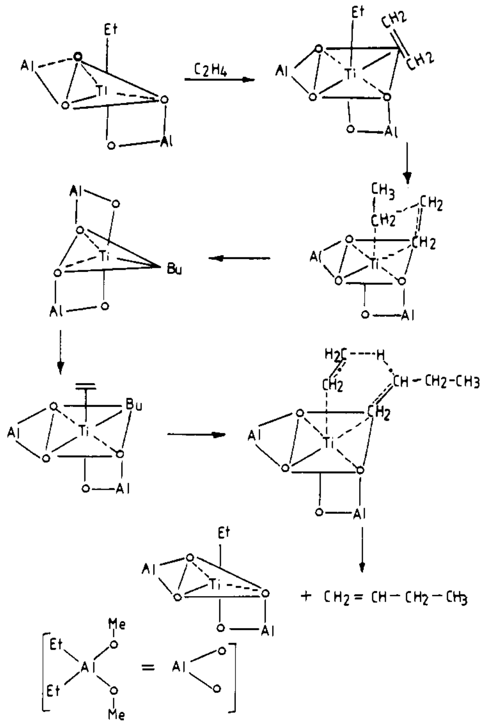
SCHEME V. Dimerization of Ethylene on Bimetallic Titanium–Aluminum Complex



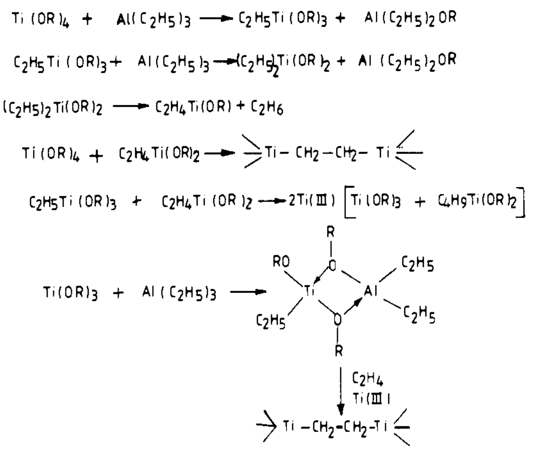
SCHEME VI. Generation of Active Catalyst from the $Ti(OCH_3)_4$–$Al(C_2H_5)_3$ System



SCHEME VII. Cossee's Mechanism for Dimerization of Ethylene by $Ti(OCH_3)_4$–$Al(C_2H_5)_3$



SCHEME VIII. Generation of Bititanium Centers from the $Ti(OR)_4$–$Al(C_2H_5)_3$ System



catalyst. Modification of the catalyst $Ti(OR)_4$–AlR_3 by additions of oxygen allows a 10–20% increase in the yield of 1-butene with simultaneous enhancement of the process selectivity. The quantity of oxygen in the reaction vessel is varied within 0.2:1 to 2:1 with regard to the quantity of alkylaluminum present therein.

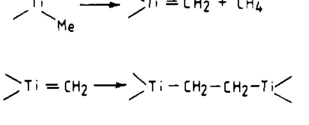
The dimerization carried out with a mixture of ethylene–hydrogen with a hydrogen concentration of 5–95% by volume results in enhanced 1-butene formation.[55]

It has been reported that with use of $AlEt_3$–$Ti(O\text{-}n\text{-}Bu)_4$ the conversion to the dimer is maximum for a Al/Ti ratio of 4:1. The activity can be increased by the addition of triphenylphosphine or phenylacetylene.[56,57]

Angelescu and co-workers[56] propose the following mechanism for the dimerization of ethylene on the bimetallic titanium–aluminum complex (Scheme V). Typical reaction conditions for the dimerization of ethylene using titanium aryl oxide–Et_3Al systems[58] are summarized in Table I.

Cossee[59] has proposed originally a mechanism for the dimerization of ethylene by the $Ti(OMe)_4$–$AlEt_3$ system. The generation of an active catalyst is given in Scheme VI. Even though the original catalyst **6** is depicted as an octahedral complex, the self-consistent all-valence electron molecular orbital calculation shows that the most stable complex is a trigonal-bipyramidal one (Scheme VII) with titanium ethyl at an intermediate position between two octahedral sites.[10,60,61] The same theoretical study shows both chain propagation and β-hydrogen transfer responsible for the alkene liberation are favored decisively by the titanium d orbitals.

Belov and his group[62,63] have proposed formation of intermediate complexes containing $>Ti–CH_2–CH_2–Ti<$ groups for the dimerization of ethylene by $Ti(O\text{-}n\text{-}Bu)_4$–$AlEt_3$ system (Scheme VIII). These behave as binuclear active centers (Scheme IX).[64] The same authors have reported that the formation of bititanium ethylene-bridged complexes in the presence of $AlMe_3$ are produced as a result of the recombination of carbeniod intermediates (eq 7). Conversion of carbeniod



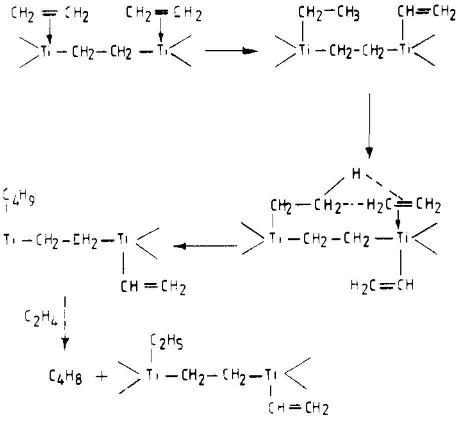
(7)

TABLE I. Typical Reaction Conditions for the Dimerization of Ethylene Using Titanium Aryl Oxide and Triethylaluminum

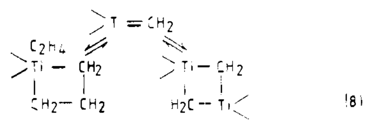
cat.	Et_3Al-$Ti(OPh)_4$	Et_3Al-$Ti(OPhMe)_4$	Et_3Al-$Ti(OPhAm)_4$
Al/Ti	3.0	3.0	5.0
solvent	*n*-heptane	*n*-heptane	*n*-heptane
Ti salt (g)	0.2280	0.2770	0.429
pressure (kg/cm^2 g)	15	15	10
temperature (°C)	40	40	75
time (min)	40	40	60
product (g)	21.2	22.6	35.7
butenes (wt %)[a]	91.5	91.3	80.2
hexenes (wt %)	5.6	5.7	17.1
polymer (wt %)	2.9	3.0	2.7
cat. activity (g of 1-butene/g of Ti salt)	85.1	74.4	67.1

[a] Selectivity to 1-butene is approximately 99%.

SCHEME IX. Dimerization of Ethylene on Bititanium Centers



species into metallacyclobutane and similar compounds (7) are more facile[65,66] (eq 8) than the recombination of carbene species as shown in eq 7 by Belov and co-workers. Thus the proposal is an unusual one and requires further investigation.


(8)

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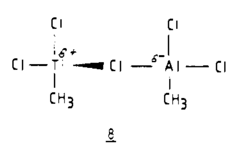
Detailed reports[67-77] on the kinetics and mechanism of ethylene dimerization by the $Ti(OR)_4$-AlR_3 system in various solvents are available. Different values of the activation energy are reported.[69,71,75]

The two-component organometallic catalyst $MeTiCl_3$-$MeAlCl_2$,[78] which is distinct from other Ti-Al systems, shows the following order of activity for the dimerization of ethylene in organic solvents: chlorinated hydrocarbons > aromatic hydrocarbons > aliphatic hydrocarbons. It exists as 8 or 9. The selectivity of the catalyst is poor in these solvents. The cationic part of the complex coordinates with the olefin, and the mechanism of the reaction is given in Scheme X.



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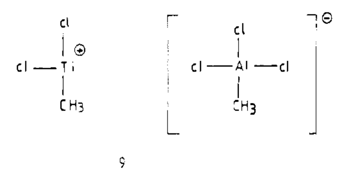

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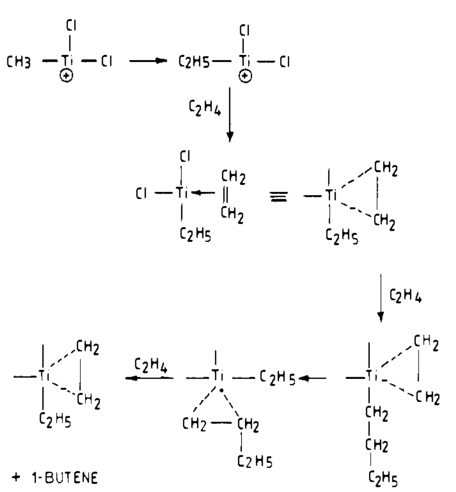
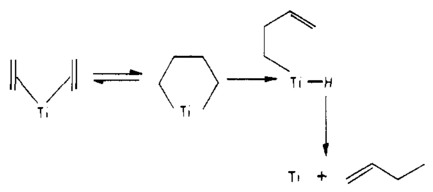
SCHEME X. Dimerization of Ethylene on the Cationic Part of Complex 9



SCHEME XI. Dimerization of Ethylene via a Titanacyclopentane Complex



Apart from the alkylaluminum compound employed in previous investigations *N,N*-dialkylaminoalanes can also be used as a cocatalyst.[79] With *N,N*-dimethylaminoalanes 95% selectivity to 1-butene is achieved.

Cyclopentadienyltitanium trichloride associated with amalgams of alkali metals[80] dimerizes ethylene to 1-butene.

Wreford and his co-workers[81] have reported that (η-$C_4H_6)_2Ti(dmpe)$ [dmpe = 1,2-bis(dimethylphosphino)ethane] catalyzes the dimerization of ethylene. A mechanism involving formation of a metallacyclopentane complex is proposed (Scheme XI). This metallacyclopentane complex decomposes to give 1-butene. This is not necessarily by the β-elimination sequence. Intermolecular hydrogen transfer and α-elimination have been suggested as alternative decomposition paths leading to 1-butene. The kinetics of the reaction shows first-order dependence on the catalyst and the olefin. Formation of a monoolefin complex is the probable rate-determining step.

In Cossee's mechanism, the stabilization of a titanium d orbital by interaction with an empty antibonding orbital of the alkene was suggested to be important for catalytic activity. There is no theoretical evidence for the d → π^* back-donation.[82] Belov's binuclear active centers are ambiguous in the light of the formation of metallacyclobutane and similar compounds. The oxidation number of titanium is important in these reactions. Ti(III) is known to be involved in polymerization. It has been pointed out[82-84] that the coordination of olefin is favored when the metal is in a higher oxidation state. Wreford and his co-worker's proposal of a concerted coupling of two molecules of ethylene to a titanium atom affording a titanium(IV)–cyclopentane species which then decomposes to 1-butene by β-hydrogen transfer explains the high selectivity to the formation of dimers. The presence of free H^+ or H^- species in the catalyst system is responsible for the isomerization of dimers.[85] The absence of any such species ensures high selectivity to 1-butene and the absence of isomerization to 2-butene.

2. Zirconium and Hafnium

A catalyst system consisting of $Zr(benzyl)_4$–$Et_3Al_2Cl_3$ at 40–80 °C shows high activity toward dimerization and oligomerization of ethylene.[20] $(\eta\text{-}C_4H_6)_2Zr(dmpe)$ through the zirconacyclopentane intermediate converts ethylene into 1-butene.[81] There are patent reports[86-88] on the use of $Zr(OR)_4$–R_xAlX_{3-x} (R = Et, Bu; X = halide) systems as catalysts between 0 and 100 °C for the dimerization reaction. Zirconium alkyls are the intermediates. They are more stable than the titanium analogues, and hence they serve as suitable catalysts for high-temperature investigations.

Du Pont[89] has patented the preparation of $(dmpe)$-MH_3 (M = Zr, Hf) and their uses as catalysts for the dimerization of ethylene.

The dimerization of ethylene induced by metallacyclopentane (M = Zr, Hf) can be explained in terms of β-hydride elimination and reductive elimination (Scheme XII).[90] *n*-Alkanes are formed by a competing sequence starting with a further β-hydride elimination from **10**, affording butadiene and the hydride complex **11**. After hydrogenation of alkene present in the solution by the hydride complex **11**, **13** is generated via **12**. The (olefin)metallocene complex **13** is trapped by the butadiene formed in the reaction cycle with formation of the catalytically inactive **14**.

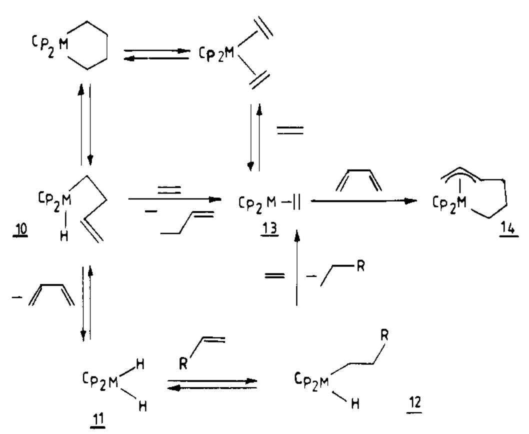
The complexes of IVB elements under optimum conditions can serve as catalysts for the dimerization and oligomerization of ethylene. It must be noted that Ti(IV), Zr(IV), and Hf(IV) do not have any 3d, 4d, and 5d electrons, respectively, to coordinate strongly with the olefin. One possibility is that the olefin behaves simply as a weak base with a lone pair of electrons. Consequently the alkene is only weakly bonded probably by overlap of s orbitals of the metal with the π orbitals of the alkene.[91] This may be an important requirement for catalysis as distinct from compound formation. The weak coordination allows the olefins to rotate to form a nonplanar transition state which is conducive to catalytic reactions.

F. Group 5 (VB) Elements

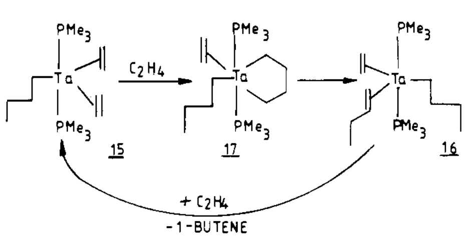
1. Vanadium

The use of vanadium trichloride for the dimerization of ethylene is patented.[92] VCl_3 and isobutylaluminum sequichloride at 60 °C and 3-atm pressure gives 1-butene (7%), *trans*-2-butene, (47%), and *cis*-2-butene (41%) along with hexenes (3%), octene (0.6%), and higher boiling distillates (1.4%).

SCHEME XII. Dimerization of Ethylene by a Bis(cyclopentadienyl) Metallacyclopentane Complex (M = Zr, Hf; Cp = η^5-C_5H_5)



SCHEME XIII. Proposed Mechanism for Ethylene Dimerization by the $Ta(CH_2C[CH_3]_3)_3(CHC[CH_3]_3)$–$2P(CH_3)_3$ System

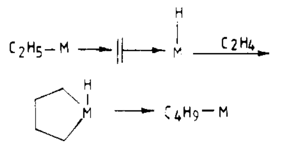


2. Niobium

The preparation of $PhNb(COD)_2$[93] and $(dmpe)_2$ NbH_5[89] and their uses as catalysts for conversion of ethylene to 1-butene have been reported in patents.

3. Tantalum

Schrock and co-workers have investigated the dimerization of ethylene catalyzed by tantalacyclopentane complexes.[9,94,95] The advantage of these complexes is that the isomerization of primary product is negligible. $CpTaCl_2(C_4H_8)$ at 40 psi of ethylene pressure gives 1-butene selectively (~3% 2-butenes).[96] On prolonged reaction ethylene/1-butene codimers are formed by the decomposition of mixed metallacycle. The authors have observed[97] that $Ta(CH_2CMe_3)_3(CHCMe_3)$ and 2 mol of trimethylphosphine produce a homogeneous catalyst which "rapidly" dimerizes ethylene selectively to 1-butene. The rate constant of this reaction is reported as approximately $k \approx 10^{-4}$ s^{-1} at 36 °C. The active component is $(C_4H_9)Ta(C_2H_4)_2$ $(PMe_3)_2$ (**15**) which is trigonal bipyramidal in geometry. The trimethylphosphine ligands are axial, and ethylene ligands are equatorial and perpendicular to the trigonal plane. The mechanism for the dimerization reaction is shown in Scheme XIII. A metallacyclopentane complex forms when ethylene attacks **15** and one of the metallacycle Ta–C(α) bonds is cleaved by a β-hydrogen atom from the butyl ligand to give **16**. The alternative possibility, viz., transfer from the metallacycle to the butyl and the ethylene ligand should be slow. The rate-determining step in this mechanism is **15** → **17**. This kind of metallacyclopentane mechanism is a plausible alternative to insertion of ethylene into a metal–ethyl bond whenever such insertion is not expected to be fast and/or when the metals in lower oxidation states are formally oxidized by forming a metallacyclopentane complex. The insertion mechanism can be viewed as proceeding through two steps which include the formation of a metallacyclopentane complex as shown in eq 9.[98] It is interesting to note that the analogous



(9)

niobium system fails to dimerize ethylene to 1-butene because of its inability to form a metallacyclopentane complex.

G. Group 6 (VIB) Elements

1. Chromium and Molybdenum

The chromium complexes $CrCl_3L_3$ and $CrCl_2L_2(NO)_2$ wherein the ligands L are pyridine and tri-*n*-butylphosphine in conjunction with ethylaluminum dichloride effect simple dimerization of ethylene at 50 °C.[99,100,101] A conversion of 4700 g of butenes per gram of chromium complex is achieved with the catalyst $CrCl_3(4\text{-}Etpy)_3$. Butene fraction consists of 1-butene (50%), *trans*-2-butene (32%), *cis*-2-butene (18%), and isobutylene (0.1%). Cr^+ or Cr^{2+} species may be involved in the reaction. Here chromium atoms are probably associated with the organoaluminum halides to form bridged chromium–halogen–aluminum species.

A chloro-bridged molybdenum complex, $[(\pi\text{-}C_6H_6)Mo(\pi\text{-allyl})Cl]_2$,[102] with ethylaluminum dichloride catalyzes the dimerization of ethylene in benzene medium at 20 °C.

2. Tungsten

Wideman[103] has reported a catalyst based on tungsten. The active catalyst is prepared by heating tungsten hexachloride and 2,6-dimethylaniline in a minimum amount of chlorobenzene and subsequently treating with diethylaluminum chloride. A conversion of 176 000 mol of ethylene/mol of tungsten is achieved in 1 h at 40 °C and 27 atm of ethylene pressure. The yield of 1-butene is 92% in the process. An increase in pressure from 27 to 34 atm resulted in the conversion of 184 000 mol of ethylene/mol of tungsten, thereby achieving a better yield of 1-butene (98%) at a faster rate.

H. Group 7 (VIIB) Elements

Manganese chloride, manganese malonate, and manganese acetylacetonate[104] with organoaluminum halides are reported to dimerize ethylene in chlorobenzene solvent. The optimum aluminum to manganese ratio is 3:1. At 45 atm of ethylene pressure and 80–85 °C, butenes consisting of 36.6% 1-butene, 42.2% *trans*-2-butene, and 21.2% *cis*-2-butene are formed.

I. Group 8–10 (VIII) Elements

1. Iron

Ferrocene and ferrous chloride along with organoaluminum halides are known to convert ethylene to a mixture of butenes at 1–20 atm and –10 to +50 °C.[105,106]

2. Cobalt

In the case of cobalt and modified Ziegler systems have limited activity toward ethylene dimerization.[30,107] Cobalt(II) or Cobalt(III) and a reducing organometallic compound system have been specially proposed for this reaction. Tris(acetylacetonato)cobalt(III) and triethylaluminum convert ethylene at 30 °C into *n*-butenes with a selectivity of 99.5%.[108] The products consist of a mixture of 95% 2-butenes and 5% 1-butene. The molar ratio of AlR_3/Co must be between 2 and 5 as beyond that the activity decreases. On the other hand, the addition of triphenylphosphine decreases the rate of reaction.

(Dinitrogen)hydridotris(triphenylphosphine)cobalt(I) has also been used to dimerize ethylene.[109] Here, the dimerization of ethylene takes place at room temperature without the use of a Lewis acid. Ethylene conversion decreases with time, presumably due to partial decomposition of the catalyst. However, this decomposition is slow at 0 °C. A mechanism is proposed in which the olefin is first inserted between the cobalt–hydride bond and then a second molecule of the olefin is inserted between the cobalt–alkyl bond. Displacement of the dimer by the olefin regenerates the cyclic process.

The dimerization of ethylene is selectively catalyzed by halotris(triphenylphosphine)cobalt(I) in halobenzene containing boron trifluoride etherate.[110,111] The catalytic activity is significantly affected by the solvent, bromobenzene being the most effective. The rate of ethylene absorption decreases in the order bromobenzene > iodobenzene > o-dichlorobenzene > chlorobenzene > o-chlorotoluene. The optimum ratio of boron to cobalt for the boron trifluoride etherate–bromotris(triphenylphosphine)cobalt(I) system is 1. This suggests a strong 1:1 interaction between the two components (eq 10). Lewis acids other than aluminum

$$CoBr(PPh_3)_3 + BF_3{\cdot}OEt_2 \longrightarrow [Co(PPh_3)_3]^+[BF_3{\cdot}Br]^- \qquad (10)$$

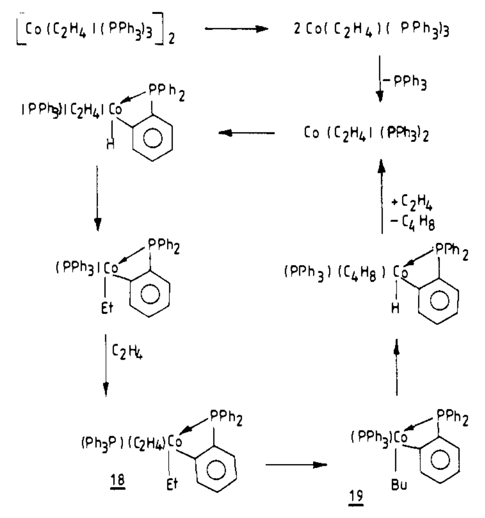
chloride and boron trifluoride etherate show no dimerization activity with cobalt complexes. Addition of triphenylphosphine and water stops the dimerization almost completely.

Speier has reported the kinetics and mechanism of the dimerization of ethylene using bis[(ethylene)tris(triphenylphosphine)cobalt] as a catalyst.[112,113] The predominant product is *trans*-2-butene (63%). The mechanism is given in Scheme XIV. Converion of 18 to 19 is the rate-determining step in this mechanism.

3. Nickel

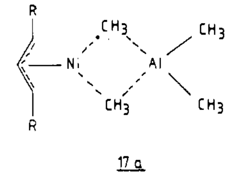
Nickel-based catalyst systems constitute one of the important catalysts for olefin dimerization because it is the only metal which can control the mode of linking of olefins. Its specific activity is high, and it is one of

SCHEME XIV. Dimerization of Ethylene by $[Co(C_2H_4)(PPh_3)_3]_2$



the less expensive of the transition elements. Because of these advantages much research has gone into the study of nickel-catalyzed dimerization.[114-140]

The discovery of the "nickel effect" represents the starting point for the development of the Ziegler catalysts.[141] A basis for the elucidation of the effect was provided by studies on the reduction of nickel compounds by organoaluminum compounds, the existence of nickel hydrides, and the interactions between nickel(0) and Lewis acids as well as organic compounds of main-group metals. Formation of multicenter bonding systems like **17a** involving trialkylaluminum compounds and nickel atoms has been demonstrated from these studies. These systems further react with coordinated ethylene molecules in a concerted manner to give butenes.

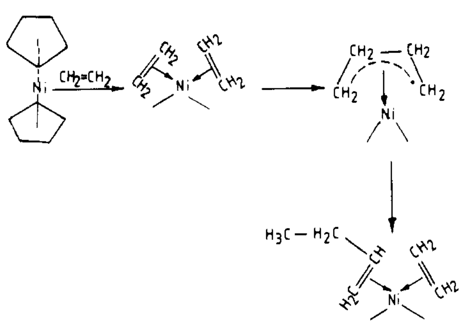


17a

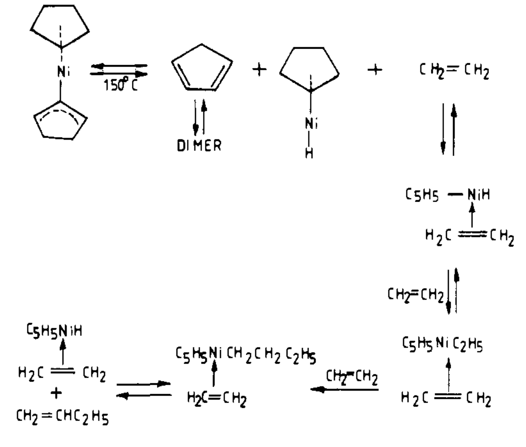
The first reports of the dimerization of alkenes by nickel complexes have been published almost simultaneously in West Germany,[142,143] France,[144] and USSR.[145,146] Ewers has used a highly active homogeneous catalyst prepared by treating $Ni(acac)_2$, $Ni(\pi\text{-allyl})_2$, or $Ni(\pi\text{-allyl})Cl$ with dialyklaluminum chloride in a toluene medium. A paper by Wilke and co-workers[147] describes the dimerization of ethylene under the influence of (π-allyl)nickel chloride in conjunction with Lewis acids and tertiary phosphines. The allyl group does not participate in the reactions.[148] It is neither displaced as in cyclooligomerization nor inserted as in polymerization but found on the nickel at the end of the reaction. Its role is probably that of a stabilizer of certain electronic states. Chauvin and co-workers[140] have used the $Ni(acac)_2$–$EtAlCl_2$ system effectively for the dimerization of ethylene.

An important feature of nickel-catalyzed dimerization is that the Lewis acid is not necessarily a reducing agent when the nickel is bonded to less than two "hard" anions ("bare" nickel, (π-allyl)nickel halide, etc.) and is a reducer when the bivalent nickel is bonded to two "hard" anions ($NiCl_2$, $Ni(acac)_2$, etc.). It may be pointed out that $Et_2Al(OEt)$ is a weak Lewis acid, and hence the system $Ni(acac)_2$–$Et_2Al(OEt)$ is less active. But in the system $NiCl_2$–PR_3–$AlCl_3$ the phosphine can play the role of a reducing agent.

SCHEME XV. Nickelocene-Catalyzed Dimerization of Ethylene



SCHEME XVI. (η^3-Cyclopentenyl)(η^5-cyclopentadienyl)nickel-catalyzed Dimerization of Ethylene

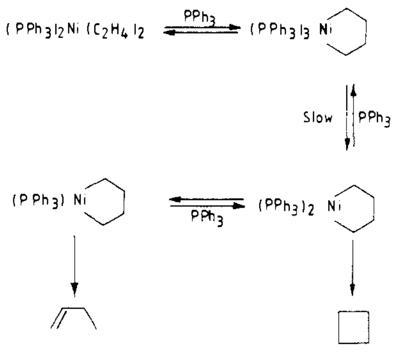


The catalytic species formed "in situ" by the reaction of Ni(II) with $R_{6-x}Al_2X_x$ are generally more active. Many attempts have been made to isolate intermediates.[149,150] Experimental observations are in agreement with the following ionic structure[151] $(Ln\text{–}Ni\text{–}H)^+A^-$, where A^- is a noncomplexing anion derived from a Lewis acid. The L may be one of the following: (a) the monomer or the dimer product, (b) a solvent molecule, (c) a component added to the catalyst system like a phosphine, or (d) any compound having a heteroatom which is capable of coordinating with the nickel.

It has been possible to dimerize ethylene by nickel in the absence of a Lewis acid. Butenes are formed by heating nickelocene to 200 °C in the presence of ethylene.[152] In this process homolytic decomposition of nickelocene produces excited nickel atoms which catalyze dimerization. This is similar to heterogeneous catalysis. In order to explain the nickelocene-catalyzed dimerization of ethylene, Tsutsui[153] has proposed a three-step mechanism (Scheme XV).

$(\eta^5\text{-}C_5H_5)Ni(\eta^3\text{-}C_5H_7)$[126] is a highly active unicomponent catalyst for the conversion of ethylene to n-butenes and n-hexenes at 145–150 °C. At high conversions of ethylene (70–90%) the dimeric product (80–86% yield) contains a high percentage (82–90%) of 1-butene. The cyclopentadienyl group remains bonded to the nickel during catalysis while cyclopentenyl group is labile. A possible mode of activation is the reversible elimination of cyclopentadiene from $(\eta^5\text{-}C_5H_5)Ni(\eta^3\text{-}C_5H_7)$ to generate (π-cyclopentadienyl)nickel hydride (Scheme XVI) as a catalytically active intermediate.

SCHEME XVII. Dimerization of Ethylene Catalyzed by Nickelacyclopentane Phosphine Complexes



Ozaki and co-workers[152] have reported dimerization of ethylene catalyzed by bis(triphenylphosphine)(pentachlorophenyl)chloronickel(II) activated with silver salts like $AgClO_4$ or $AgBF_4$. The activity is enhanced by adding a catalytic amount of PPh_3 ($PPh_3/AgClO_4 \leq 1$). An excess of PPh_3 ($PPh_3/AgClO_4 \leq 2$) stops ethylene dimerization. Separate runs show that $AgNO_3$, $NaClO_4$, and $NaBF_4$ do not activate the catalyst. Enhancement of the activity of the complex by a catalytic amount of PPh_3 may be attributable to an increase in the solubility of $AgClO_4$. Contrary to the PPh_3 complex, the phenyldimethylphosphine complex is much less active for ethylene dimerization.

$(C_6H_5)Ni(PPh_3)_2Br$ gives a maximum activity for ethylene dimerization when the molar ratio of added $AgClO_4$ to the complex reaches 2.[154] ^{31}P NMR study of the reaction between $AgClO_4$ and the complex reveals that the variation in dimerization activity becomes parallel with the concentration of $(C_6H_5)Ni(PPh_3)ClO_4$ formed in the reaction. The coordinatively unsaturated state of the complex will be one of the reasons for its catalytic activity. The role of $AgClO_4$ is to remove of halogen and PPh_3 from the original complex although excessive removal of ligands results in the formation of an inactive complex.

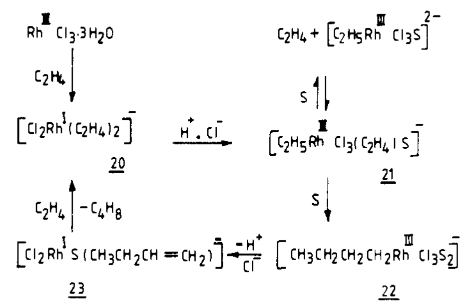
Nickel phosphine metallacyclopentanes especially tris(triphenylphosphine)tetramethylenenickel(II) catalyze the production of cyclobutene and 1-butene from ethylene.[155] The course of the reaction is depicted in Scheme XVII.

The oligomerization of ethylene with a heterogeneous catalyst of a polystyrylnickel phosphorous ligand complex is carried out, and the result is compared with that of the oligomerization of ethylene with a homogeneous catalyst of $Ni(acac)_2$–$Et_3Al_2Cl_3$–phosphorous ligand.[156] When PPh_3 is used as a phosphorous ligand, the homogeneous catalyst gives a considerable amount of trimer together with the dimer but the heterogeneous polystyrylnickel catalyst yields only butenes with mainly 1-butene. The results are discussed in terms of the steric and electronic effect of a phosphorous ligand and the steric effect of the catalyst support (i.e., polystyryl chain).

$Ni(PPh_3)_4$ anchored on brominated polystyrene on activation by $BF_3 \cdot OEt_2$ exhibits high dimerization catalytic activity for ethylene.[157] The catalyst is reused without loss of activity.

Despite the instability of the catalytic system at low temperature a kinetic study has been carried out in the case of $NiCl_2$(tetramethylcyclobutadiene)–$EtAlCl_2$–$P(n\text{-}Bu)_3$ for the dimerization of ethylene.[158] The reaction is second order with respect to monomer and first order with respect to nickel but is of a complex order with respect to aluminum compounds. The overall activation energy lies between 7 and 9 kcal/mol. Kinetics of ethylene dimerization in the presence of heterogenized (π-allyl)nickel complexes is also investigated.[159]

SCHEME XVIII. Dimerization of Ethylene under the Influence of Rhodium Chloride in Alcoholic Hydrogen Chloride Solutions (S = Cl⁻, H_2O, or Solvent)



4. Ruthenium

$RuCl_3$ in methanol medium is reported to be a dimerization catalyst for ethylene but with poor selectivity and activity.[160] When $RuCl_3$ is heated with 500–800 atm of ethylene at 130 °C for 10 h, 2-butenes are formed along with hexenes, octenes, and higher olefins.[161]

5. Rhodium

Rhodium chloride is active in the dimerization of ethylene at 30–50 °C.[155]

Cramer[162] has made a detailed study of the dimerization of ethylene under the influence of rhodium chloride in alcoholic hydrochloric acid solutions and proposed the mechanism as shown in Scheme XVIII. Activation of catalyst occurs by the reaction between $RhCl_3$ and ethylene with formation of a complex anion (**20**) of univalent rhodium with two ethylene ligands. A fast protonation of **20** gives the ethyl complex **21**, and the insertion of a coordinated ethylene at the rhodium–carbon σ-bond (the rate-determining step) gives the butyl complex **22**. This is rapidly converted into a complex, **23**, from which a molecule of butene is replaced by ethylene regenerating the starting complex **20**. The solvent molecules are introduced into the reaction pathway in order to satisfy the coordination numbers of Rh(I) and Rh(III).

However, Schrock and co-workers[97] have proposed that the crucial intermediate in Cramer's ethylene dimerization system could be a metallacyclopentane complex and the butyl complex is formed as a result of its protonation (eq 11). The rate of dimerization of

$$[Cl_3(C_2H_4)\underbrace{Rh\,CH_2\,CH_2\,CH_2\,CH_2}]^{2-} \xrightarrow[\text{Solvent}]{H^+} [Cl_3(C_2H_4)Rh(C_4H_9)S]^- \quad (11)$$

$$\frac{d[C_4H_8]}{dt} = k[C_2H_4][\overset{+}{H}][Cl^-][Rh] \quad (12)$$

ethylene is described by Cramer[162] by eq 12. It is also possible to dimerize ethylene by a nonionic reaction using $(\pi\text{-}C_2H_4)Rh(C_2H_4)_2$ as a catalyst, but the reaction is not fast.

Keii and Okura have studied the kinetics of ethylene dimerization with rhodium catalysts such as $RhCl_3$ and $Cl_2Rh_2(C_2H_4)_2$.[163] The rate of butene formation in the presence of $RhCl_3$ is represented by eq 13.

$$R = \frac{kKp^2C}{1+kp^2} \quad \text{where}$$

C = concentration of catalyst -------------- (13)

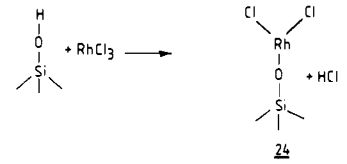
p = Ethylene pressure

k,K = Constants

EHMO calculations for the dimerization of ethylene on Rh^+ and Rh^{3+} ions have been carried out.[164] In all stages of reaction Rh^{3+} exhibits greater catalytic activity than Rh^+.

Rhodium chloride supported on silica gel is found to be more active than the homogeneous catalyst for ethylene dimerization.[165,166] As in the homogeneous catalyst hydrogen chloride remarkably enhanced the catalytic activity. 1-Butene formed in initial stage is isomerized to 2-butene. The dimerization activity per unit weight of catalyst increases in the order silica gel supported > silica–alumina supported > alumina supported.

The active rhodium species of the supported catalysts is the surface compound **24** formed from rhodium chloride and the surface silanol according to eq 14.



(14)

The high dimerization activity is due to the ligand effect of Si–O– on rhodium. Activation energy for the dimerization is calculated as 7 kcal/mol which is about half of that obtained by using the homogeneous catalysts.

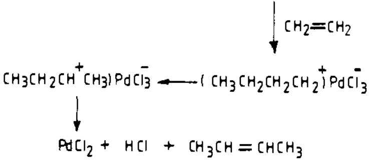
$[Rh(SnCl_3)_2Cl_4]^{3-}$ immobilized on AV-17-8 anion-exchange resin is highly active, stable, and selective catalyst for the dimerization of ethylene to *cis*- and *trans*-2-butenes in acidic media.[167] A mathematical model is derived to describe the process in terms of the ethylene pressure, temperature, and reaction time. The optimum yield of butenes is 88%. A cis/trans ratio of 1:2.7 is obtained after 6 h at 75 °C and 42 atm of ethylene.

6. Palladium

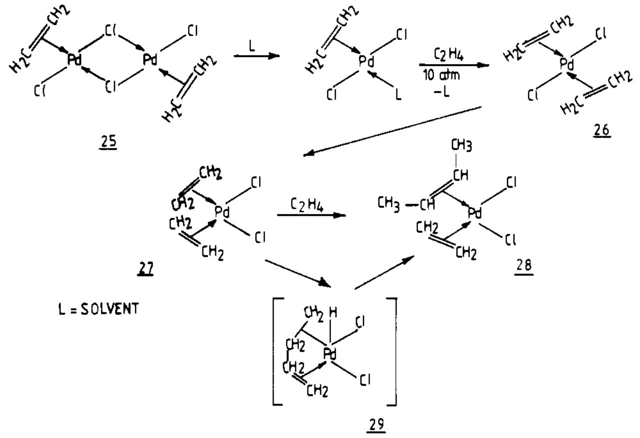
Use of palladium complexes in ethylene dimerization is less prevalent presumably because of its low activity and high cost.

Palladium chloride dimerizes ethylene at 20–70 °C and 1–40 atm to yield butenes with 90% selectivity.[168] It has been suggested that this compound initiates the dimerization in the presence of hydrogen chloride by a mechanism (Scheme XIX) analogous to that of Friedel–Crafts catalysis.

SCHEME XIX. Dimerization of Ethylene Catalyzed by $PdCl_2$ in the Presence of Hydrogen Chloride



SCHEME XX. Dimerization of Ethylene by $PdCl_2$

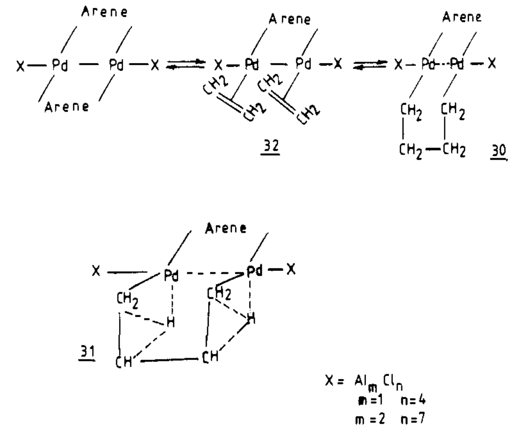


The dimerization of ethylene into *n*-butenes by means of tetrachlorobis(ethylene)dipalladium in nonhydroxylic media (benzene or dioxane) has been attempted.[169] Other palladium salts (fluoride, bromide, iodide, nitrate) tested in the dimerization of olefins do not form complexes of the type $(C_2H_4)_2Pd_2X_4$. Palladium cyanide dimerizes ethylene twice as slowly as $PdCl_2$, probably on account of deactivation of the catalyst by a polyethylene deposit formed along with the dimer.[6]

The solvents used in these dimerization reactions dictate the activity of the catalysts. Besides benzene and dioxane, acetic acid,[169,170] halogenated hydrocarbons,[168,170,172] nitro derivatives,[170,171] sulfones, tetrahydrofuran, ethyl acetate, phenol, dimethylformamide, hydroquinone, catechol, benzyl alcohol, salicyclic acid, anisole, and acetone[170] have been used. On solvents like benzene and chlorohydrocarbons and in highly polar solvents like dimethyl sulfoxide and dimethylformamide dimerization does not occur. The reaction proceeds smoothly in solvents containing oxygen atoms. The dissociative solvents like phenol and acetic acid show high solvent effects. In carboxylic acids the rate of dimerization decreases with an increase in pK_a. Use of deuterated acetic acid as a solvent shows that the dissociated anion is taking part in the reaction. The rate of reaction follows the order weakly dissociative solvent > dissociative solvent > nondissociative solvent.

An important contribution to the mechanism (Scheme XX) of the dimerization by palladium is due to Ketley and co-workers.[170,171] According to them in the first step solvents like ethanol acting as weak ligands or additives will cause the opening of the chloride bridges of the Kharasch complex **25** resulting in the formation of complex **26** under a positive pressure of ethylene. Now complex **26** can undergo geometric isomerization bringing the two ethylene molecules into position next to each other. The detailed mechanism of the conversion of **27** to **28** is far from clear, no evidence having been obtained of an intermediate metal hydride. Ketley and his co-workers have postulated the transient formation of a Pd–H species. This can arise from a vinylic hydrogen abstraction by the metal (**27** → **29** → **28**).

SCHEME XXI. (η-Arene)$PdAl_mCl_nL_2$-catalyzed Dimerization of Ethylene



The dimerization of ethylene by $Pd(BzCN)_2Cl_2$ has been reported by Barlow and Bryant.[173] Dimerization and the accompanied isotopic exchange of ethylene have been studied with $Pd(BzCN)_2Cl_2$ in benzene.[174] Both the reactions take place after an induction period, the extent of which is reduced by the presence of a hydrogen releasing olefin such as 3-methyl-1-butene. The kinetics of dimerization is first order in ethylene, and the rate does not immediately respond to change in ethylene pressure. The reaction product is exclusively butenes with a composition of 1-butene (4%), *cis*-2-butene (36%), and *trans*-2-butene (60%) which is close to the value corresponding to the equilibrium of isomerization.

(η-Arene)$PdAl_mCl_{n-2}$ (arene = benzene, toluene, *p*-xylene, $m = 1$, $n = 4$; arene = benzene, $m = 2$, $n = 7$) catalyzes the dimerization of ethylene (85–90%) at room temperature.[175] The suggested mechanism (Scheme XXI) for this reaction involves the substitution of one arene unit by ethylene followed by coupling of two ethylene molecules. The evolution of **30** can be supported to proceed through a hydride transfer process (**31**) producing butene and, in the presence of ethylene, again **32**.

Palladium chloride supported on silica gel and γ-alumina are active for the dimerization of ethylene.[176] $PdCl_2(Me_2SO)_2$[177–179] and $K^+PdCl_3^-(Me_2SO)$ on KSH-2 silica gel[179] catalyze ethylene dimerization. The yield of dimer and selectivity are high with use of 0.1% dimethyl sulfoxide complex precipitated from acetone at 90 °C and with 0.3% ionic complex precipitated from chlorobenzene at 100 °C.

7. *Iridium and Platinum*

$IrCl_3$ in alcohol medium is capable of dimerizing ethylene to 95–99% 2-butene and 1–5% 1-butene.[161]

$Pt(PPh_3)_4$ supported on heterogenized polystyrene[180] or *p*-chlorostyrene–diviynlbenzene copolymers along with $BF_3{\cdot}OEt_2$ in hexane medium dimerizes ethylene to a mixture of butenes.

Table II summarizes the available published and patent literature. Some representative kinetic data for the dimerization of ethylene are also summarized in Table III.

IV. Catalytic Dimerization of Propylene Using Transition-Metal Complexes

The versatality of the dimerization of propylene is very much evident from the fact that the products individually or a mixture of them find extensive applications. The dimerization of ethylene essentially involves the addition of a C–H bond of one olefin molecule across the double bond of a second one. On the other hand, in the dimerization of propylene four products can be possible if only the vinylic C–H bonds are considered, two products involving a C–H bond of the methylene carbon and another two products involving a C–H bond of the methine carbon. The major products of dimerization are *n*-hexenes, 4-methylpentenes, 2-methylpentenes, and 2,3-dimethylbutenes. The selectivity of the products depends upon the metal, the ligands, and the mode of activation of the olefin.

Pilot scale as well as industrial scale (IFP dimersol process) dimerization of propylene using organometallic catalysts have been reported.[350,351] The product compositions, mechanisms, and reaction conditions of this reaction are discussed together with the various homogeneous and supported metal complex catalysts.[32,113,140,352–361]

A. Group 11 (IB) and 12 (IIB) Elements

$CuAlCl_4$ and Cu_2Cl_2 in the presence of Et_2AlCl[33] in isooctane medium catalyzes the dimerization of propylene at atmospheric pressure to give *trans*-4-methyl-2-pentene (30.4%), hexenes (27.4%), and 2-methyl-2-pentene (29.9%) as major products and *cis*-4-methyl-2-pentene (4.5%), 2-methylpentane (1.3%), 4-methyl-1-pentene (1%), and 2-methyl-1-pentene (0.6%) as minor products. $AgAlCl_4$ and $ZnAl_2Cl_8$ with $EtAlCl_2$ or Et_2AlCl is also used for conversion of propylene to *trans*-4-methyl-2-pentene and 2-methyl-2-pentene.

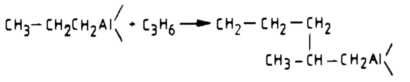
B. Group 13 (IIIA) Elements

1. *Boron*

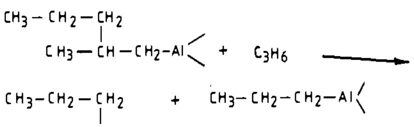
A patent report[359] is available on the dimerization of propylene in presence of $BBu_3–MR_{n-m}H_m$ (M = Al, Ga, In, Be, Mg, Zn; R = monovalent hydrocarbon radical; n= valence of metal; m = 0–3) at 195–200 °C. Organoborane promotes the isomerization of the product to an α-olefin which is stabilized by shifting an alkyl group to form selectively 2-methyl-1-pentene.

2. *Aluminum*

The dimerization of propylene by alkylaluminum proceeds via carbanion intermediate.[151] In the reaction between propylene and Al-*i*-Pr_3 initially an unstable alkylaluminum compound is formed[360] (eq 15). This then reacts with propylene according to eq 16.



$$CH_3{-}CH_2CH_2Al\langle + C_3H_6 \rightarrow \begin{array}{l} CH_2{-}CH_2{-}CH_2 \\ \qquad\quad | \\ CH_3{-}CH{-}CH_2Al\langle \end{array} \qquad (15)$$



$$\begin{array}{l} CH_3{-}CH_2{-}CH_2 \\ \qquad\quad | \\ \quad CH_3{-}CH{-}CH_2{-}Al\langle \end{array} + C_3H_6 \longrightarrow \begin{array}{l} CH_3{-}CH_2{-}CH_2 \\ \qquad\quad | \\ CH_3{-}C{=}CH_2 \end{array} + CH_3{-}CH_2{-}CH_2{-}Al\langle \qquad (16)$$

If the propylene dimer 2-methyl-1-pentene is taken out of the reaction mixture, the mechanism of the process becomes catalytic and a small amount of the alkylaluminum compound will be sufficient to dimerize the propylene.[361-363] In the dimerization of propylene at high temperatures and pressures using a $AlPr_3$ catalyst, it is reported that the integrated contact number K_0 is the most convenient and reliable control parameter for the automatic process control.[364] It determines both the selectivity of the process and the degrees of conversion. Calculations and experimental data show that optimum process conditions are achieved at $K_0 \approx$ 2–4.

Schmidt and co-workers[365] have reported the effect of organoaluminum compounds on the catalytic properties of complex catalysts used in the dimerization of propylene. The selectivity for the process is strongly dependent on temperature, pressure, and contact time.[362,366-368] In a continuous process of the dimerization of propylene at 200 atm with $AlEt_3$ activation it is observed that the yield of dimer increases with temperature.[369] Studies on the dimerization kinetics[370,371] have shown that the reaction order with respect to propylene is close to unity. Activation energies of 11.7[370] and 14 kcal·mol^{-1} [371] have been reported.

The Ziegler dimerization of propylene is used as the first stage in the production of isoprene from propylene.[362,366-368,372] The Goodyear Tire and Rubber Co., which produces 2-methyl-1-pentene on an industrial scale, has carried out extensive research on the use of a propylene dimer as a starting material in the industrial synthesis of isoprene.[373]

C. Group 14 (IVA) Elements

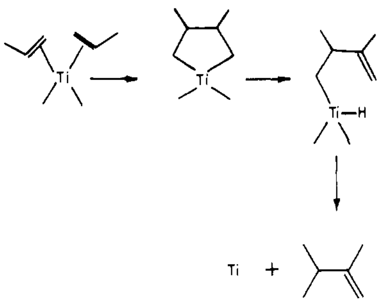
There is a patent[33] on $PbAl_2Cl_8$–$EtAlCl_2$ or Et_2AlCl catalyzed dimerization of propylene to *trans*-4-methyl-2-pentene and *n*-hexenes. Higher activities at moderate temperatures and pressures are observed when compared with other Friedel–Crafts catalysts.

D. Group 4 (IVB) Elements

1. *Titanium*

Propylene dimerization has been achieved[46] by using an AlR_3–$Ti(OR)_4$ system with an $AlR_3/Ti(OR)_4$ ratio < 10. Ti(acac)$(OR)_3$, where R = butyl or isopropyl, with $AlEt_3$[374] at 60 °C under 8.5 atm of propylene gives 4-methyl-1-pentene (43%), 4-methyl-2-pentene (1.6%), *n*-hexene (9%), and 2-hexene (46.4%). $(\eta\text{-}C_4H_6)_2$Ti(dmpe) catalyzes the dimerization of propylene to 2,3-dimethyl-1-butene, suggesting metallacycle formation (Scheme XXII) as an intermediate in the reaction.[81]

SCHEME XXII. Dimerization of Propylene Catalyzed by $(\eta\text{-}C_4H_6)_2$Ti(dmpe)



The dimerization of propylene occurs as a side reaction during propylene polymerization using titanium trichloride catalyst.[375] Several possible mechanisms of dimer formation are discussed. In the presence of a commercial catalyst dimer formation is 50–100 times higher than that in the presence of microspherical $TiCl_3$ catalyst obtained in the laboratory by reduction of $TiCl_4$.

2. *Zirconium*

$(\eta\text{-}C_4H_6)_2$Zr(dmpe)[81] dimerizes propylene to 2,3-dimethyl-1-butene by a process similar to the titanium analogue. A process for the conversion of propylene to C_6 and higher α-olefins by (π-allyl)$ZrBr_3$ and (benzyl)$ZrBr_3$ in the presence and absence of Et_2AlCl or $EtAlCl_2$ has been reported.[332] Zirconium(IV) acetylacetonate with $Et_3Al_2Cl_3$ and PPh_3 or PBu_3 at 65 °C catalyzes the dimerization of propylene.[376] Molar ratios of monophosphine to zirconium of about 1–10:1 and Lewis acid to zirconium of 1–40:1 are preferred. Use of multifunctional phosphines such as a 1,2-bis(diphenylphosphino)ethane in place of the unidentate phosphine in the catalyst composition shows no catalytic activity for the dimerization of propylene. Apart from zirconium(IV) acetylacetonate zirconium salts of cyclic and aromatic carboxylic acids like zirconium cyclohexene carboxylate, zirconium phenylacetate, zirconium benzoate, and zirconium phthalates can be used.

E. Group 5 (VB) Elements

1. *Niobium*

There is a patent on the $RR^1{}_nR^2NbA_m$ (R = cyclopentadienyl: R^1 = benzyl; n = 0, 1; R^2 = Me_3CCH, PhCH; A = halogen; *m* = 1, 2)–$YR^3{}_3$ (Y = N, P, AS, Sb, Bi; R^3 = alkyl, aryl) catalyzed dimerization of propylene in decane medium.[377]

2. *Tantalum*

β,β'-Disubstituted and α,β'-disubstituted tantalacyclopentane complexes are intermediates in the se-

TABLE II. Selected Studies on Dimerization of Ethylene by Transition-Metal Complexes

cat.	reactn condtn	products	comments	ref
Aluminum				
$(C_2H_5)_3Al$	gas phase, 160–230 °C	1-butene, 2-butenes		35
$(C_2H_5)_3Al$–Ni salts		1-butene		39, 181
$(C_2H_5)_3Al$		1-butene, C_6 and C_8 alkenes	conversn >20%	43
$(C_2H_5)_3Al$–$(C_2H_5)_2AlX$ (X = halogen or alkoxy group)	hydrocarbon solvents	1-butene, α-olefins containing up to 20 carbon atoms		182
$(C_2H_5)_3Al$	ethylene = 500 psig. 125 °C, 5.5 min	1-butene (48.9%), 1-hexene (31.1%), 1-octene (16.4%), C_{10}–C_{14} α-olefins (3.5%)		183
$R_xAlR'_{3-x}$–$R_2SnR'_2$ ($x = 2$; R = alkyl; R′ = halogen)	ethylene = 450 psig, nonane, 100–105 °C, 1.5 h	1-butene (31%), *trans*-2-butene (36%), *cis*-2-butene (20%)		184
R_3Al (R = C_{1-6} alkyl or aryl)	hydrocarbon solvents	1-butene, hexenes		185, 186
$(C_2H_5)_3Al$–$(i\text{-}C_4H_9)_3Al$	tetradecane, 700 psi, 126 °C, 30 min	1-butene (22.0%), 1-hexene (58.7%), 1-octene (16.6%), 1-decene (2.6%)		187
Titanium				
$Ti(OR)_4$–$(C_2H_5)_3Al$		1-butene (60–99%), 2-butenes		44, 188, 189, 190, 191
$Ti(OR)_4$–R_3Al		1-butene, 2-butenes	$R_oAl/Ti(OR)_4 < 10$; high selectivity to 1-butene	46
$Ti(O\text{-}n\text{-}Bu)_4$–$(C_2H_5)_3Al$	*n*-heptane, 6–8 h, 60 °C	1-butene, hexenes		45
$Ti(OBu)_4$–$(C_2H_5)_3Al$–PPh_3 or –PhC≡CH	toluene, argon, 0–20 °C	1-butene	max activity at Al/Ti = 4	56
$Ti(OBu)_4$–$(i\text{-}C_4H_9)_3Al$		1-butene	Al/Ti = 4; selectivity = 95.69	57
$Ti(OBu)_4$–$(C_2H_5)_3Al$	toluene or *n*-heptane, 20 °C	1-butene	$Ti(OBu)_4/(C_2H_5)_3Al = 10$; selectivity = 98.9%	62, 70
$Ti(OR)_4$–R_3Al–additives		1-butene, 2-ethyl-1-butene, 3-methyl-1-pentene		58, 76, 192
$Ti(OBu)_4$–R_3Al (R = Me, Et, Me_2CHCH_2)	*n*-heptane	1-butene, hexene, and polymers	$(C_2H_5)Al/Ti(OBu)_4 = 4$; E_a = 38 kcal/mol	69, 72, 193
$Ti(O\text{-}i\text{-}Pr)_4$–$Al(C_2H_5)_3$	*n*-heptane, 7.12 atm. 90 °C, 120 min	1-butene (>90%), 2-butenes (~1.5%), hexenes (2–4%), polyethylene	Al/M = 5.6; butene-1 yield is 720 g/g of cat.	194
$Ti(OBu)_4$–$(C_2H_5)_3Al$	diethyl ether or dibutyl ether, 3 h	1-butene	3 kg of 1-butene/g of $Ti(OBu)_4$	67, 195, 196, 197
$Ti(OBu)_4$–$(C_2H_5)_3Al$	pentane (27–37 °C), 40–60 °C	1-butene	Al/Ti = 3	198
$Ti(OBu)_4$–$(C_2H_5)_3Al$	pentane/isopentane	1-butene, hexenes, higher olefins	solv/cat. wt ratio is 10–1000:1	199
$Ti(OBu)_4$–$(C_2H_5)_3Al$–Ph_3CCl	*n*-heptane or dichloroethane, 20 °C	1-butene	E_a = 11.3 kcal/mol	71
$Ti(OR)_4$–R_3Al–electron donor additives	polar solvents	1-butene	selectivity is high with polar solvents and electron donor additives	73
$Ti(OBu)_4$–$(CH_3)_3Al$	deuterated ethylene	1-butene, deuterated butenes		74
$Ti(OBu)_4$–R_3Al (R = alkyl, aryl)	hydrocarbon solvents, 0–100 °C, 0.2–15 atm	1-butene		200
$Ti(OR)_4$–R_3Al (R = normal and branched alkyls)	ethyl chloride	1-butene	selectivity to 1-butene is 98%; E_a = 12.6 kcal/mol	75, 201
$Ti(OR)_4$–R'_3Al (R = Bu, Pr, pentyl, phenyl; R = isobutyl, propyl, ethyl)		1-butene	activity of cat. is of the order when R = butyl > pentyl > propyl > isopentyl > phenyl; selectivity of the catalyst is in the reverse order	58, 202, 203
$Ti(OR)_4$–R'_3Al (R = C_2H_5, C_3H_7, C_4H_9, C_6H_{14}, C_6H_{13}, C_7H_7, C_2H_4Cl; R′ = C_2H_5, C_4H_9)	ethyl chloride	1-butene	for $(C_2H_5)_3Al$–$Ti(OBu)_4$ system 98% selectivity for 1-butene production	77
$(BuO)_nTi(ac)_{4-n}$ (n = 2, 3;	CH_2Cl_2 or toluene,	1-butene (65%), hexenes (35%)	order of reactivity is	78

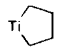
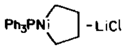
ac = acetylacetonato)/ $TiCl_4$–$(CH_3)_3Al_2Cl_3$	*n*-heptane, −100 °C		halogenated hydrocarbons > aromatic hydrocarbons > aliphatic hydrocarbons	
$Ti(O\text{-}n\text{-}Bu)_4$–$[(CH_3)_2CH]_3Al$	cyclohexane, ethylene = 500 psi, 75 °C, 26 min	1-butene, 2-butenes, polymer		204
C_pTiCl_2–amalgams of alkali metals	5 kg/cm², 30–32 °C, 4–5 h	1-butene (80–88%), 1-hexene (12–20%)		80, 205, 206, 207
C_pTiCl_2–$(C_2H_5)_3Al$–$Ti(O\text{-}n\text{-}Bu)_4$	heptane/decane/toluene	1-butene (88–95%)		54
$(\eta\text{-}C_4H_6)_2Ti(dmpe)$		1-butene, *cis*-2-butene, 3-methyl-1-pentene, 2-methyl-1-pentene		81
	toluene, 70 °C, 30 min	*n*-butane (7%), 1-butene (15.4%), *cis*- and *trans*-2-butene (46%), butadiene (31.6%)		90, 208
$Ti(OR)_4$–R'_3Al (R = Bu; R′ = hexyl, Et, Bu, *i*-Bu)	diesel oil, *n*-heptane, ethylene = 1–10 atm, 20–100 °C	1-butene (60–99%), the remainder is 2-butenes and small amounts of *n*-hexenes		209, 210, 211, 212
$Ti(O\text{-}n\text{-}Bu)_4$–$R_3Al$	*n*-heptane, H, O, N, or inert gas pretreatment of catalyst	85% 1-butene with air treatment, 80% 1-butene without pretreatment		55, 213
$Ti(O\text{-}n\text{-}Bu)_4$–$(C_2H_5)_3Al$	*n*-heptane, hydrogen and ethylene mixture = 2.5 atm, 57 °C, 1 h	1-butene (77.6%), hexenes (22.0%), polymer (0.4%)		214
titanium alcoholate–R_3Al	0.2–2.0 equivalent of oxygen based on cocatalyst; organic solvent	1-butene		215
$Ti(OBu)_4$–$(C_2H_5)_3Al$–$CH_3OCH_2CH_2OCH_3$	pentane	1-butene, mixture of hexenes		216
$Ti(OR)_4$–R_3Al–$C_3H_7OH/C_4H_9OH/C_6H_5OH$		1-butene		217
$Ti(O\text{-}n\text{-}Bu)_4$–$(C_2H_5)_3Al$–$P(OBu)_3$	*n*-heptane, 50 °C, ethylene = 20 atm	1-butene (99.5%), polymer (0.1%)	Al/Ti = 6.5 and P/Ti = 3	218
$Ti(OR)_4$–R_3Al–oxygen/amines	*n*-heptane	1-butene, higher olefins, polymer	312 g of 1-butene/g of $TiEt(OBu)_3$	219, 220, 221
$Ti(OR)_4$ (R = $C_{1\text{-}6}$ alkyl or aryl)	hydrocarbon solvents	1-butene, mixture of hexenes	80–345 g of 1-butene/g of $Ti(OR)_4$/h	185
$Ti(OR)_4$–R_3Al–C_pTiCl_2/o-phenylenediamine	ethyl chloride, C_2H_4 = 3 atm, 30 °C, 90 min	1-butene, small amounts of (1.78) polymer and 2-butenes	260 g of 1-butene/g of $Ti(OBu)_4$	222, 223, 224
$(BuO)_3Ti(C_2H_5)$–$(C_2H_5)_3Al$; $(PhCH_2O)_4Ti$–$(C_2H_5)_3Al$; $Ti(OBu)_4$–$HAl(i\text{-}Bu)_2$	heptane/decane/toluene/ether/THF	1-butene (88–95%)		54
$Ti(OR)_4$–$H_2AlNMe_2/H_2AlNBu_2/HAlClNBu_2$	toluene, 65–70 °C, 20–60 atm, 3 h	1-butene (94%)		225
$Ti(OR)_4$–$(C_2H_5)_3Al/AlH(i\text{-}C_4H_9)_2$	*n*-heptane/*n*-decane/ethyl chloride, 20–40 °C, 0.55–10 atm, 96–120 min	1-butene (94.7%), higher olefins, polyethylene (5.3%)		226
$Ti(OC_2H_5)_2(acac)_2$–$(C_2H_5)_3Al$	heptane, 7.12 atm, 90 °C, 120 min	1-butene	Al/M molar ratio = 6.1, 1-butene yield is 38 g/g of cat.	227
$Ti[N(CH_3)_2]_4$–$(C_2H_5)_3Al$	heptane, 7.12 atm, 90 °C, 120 min	1-butene	Al/M molar ratio = 2.9, 1-butene yield is 35 g/g of cat.	227
$(\pi\text{-}C_5Me_5)Ti(OR)_3$–$(C_2H_5)_3Al$	isopropylcyclohexane, 30 °C, 3 h	1-butene (>90.9%), hexenes (7.9%), butane (1%)	Al/Ti ratio = 3:1	228
$(OR)_3Ti(acac)$–R_3Al–R_2HAl	heptane, 30 °C, 2 h, ethylene = 5 kg/cm²	1-butene		229
L_2TiH_3 (L = $Me_2PCH_2CH_2PMe_2$)		butenes		89
$Ti(OR)_4$–organoaluminum–$PR''(OR')_2$ (R″ = thionyl; R′ = alkyl)	organic solvent	butenes	cocat./additive = 0.1–1.0	230

TABLE II (Continued)

cat.	reactn condtn	products	comments	ref
		Vanadium		
VCl_3–(i-$C_4H_9)_3Al_2Cl_3$	heptane, 30 min, 60 °C, 3 atm	1-butene (7%), *trans*-2-butene, (47%), *cis*-2-butene, (41%), hexenes (3%), octene (0.6%), higher olefins (1.4%)		92
VO(O-*i*-Pr)$_3$–$(C_2H_5)_3Al$	heptane, 7.12 atm, 90 °C, 160 min	1-butene	Al/M molar ratio = 3.8, yield 80 g/g of cat.	227
		Chromium		
$(C_5H_5N)_3CrCl_3$/(4-$EtC_5H_4N)_4CrCl_3$/ $[(PBu_3)_3CrCl_3]_2$/$(Ph_3PO)_3CrCl_3$/ Cl_2(4-$EtC_5H_4N)_2Cr(NO)_2$– $(C_2H_5)AlCl_2$	17 °C, 750 psig, 1 h	butenes (82%)		99, 100, 101
		Manganese		
$MnCl_2$/Mn malonate/Mn acetylacetonate/$MnSO_4$/$Mn(NO_3)_2$/ $Mn(OMe)_2$–$(C_2H_5)AlCl_2$/ $(C_2H_5)_3Al_2Cl_3$/Br_3Al/$(C_2H_5)_3Al$	chlorobenzene, argon, 50 kg/cm^2, 80–85 °C, 1 h	1-butene (36.6%), *trans*-2-butene (42.2%), *cis*-2-butene (21.2%)	Mn/Al ratio = 1:3	104
		Iron		
R_pFe–R'_mAlX_{3-m}–phosphine (R = acyl, allyl, cyclopentadienyl; p = valency of metal; R' = alkyl; X = halogen; m = 1, 2, or 3)	*n*-heptane/benzene, –50 to 150 °C, 1–25 atm	butenes		105
$FeCl_2$–$R_3Al_2X_3$ (R = alkyl; X = Cl, Br)	chlorobenzene, argon, 30 kg/cm^2, 60–70 °C, 15 min	1-butene, *trans*-2-butene, *cis*-2-butene		106
		Cobalt		
Co(acac)$_3$–$(C_2H_5)_2Be$	toluene, 8 kg/cm^2, 30 °C, 1 h	1-butene (4%), 2-butene (96%)		231
Co(acac)$_3$–BuLi	benzene	butenes	max conversn with 6:7 Li/Co(III)	232
Co(acac)$_3$–$(C_2H_5)_3Al$–PPh_3	30 °C	2-butenes (95%), 1-butene (5%)	selectivity is 99.5%; AlR_3/Co = 2–5	108, 130
Co(acac)$_2$–BuLi	benzene, 30 °C, 50 psig, 4 h	butenes	3:1 Li/Co(III) gives 4 mol of butene whereas 5:7 Li/Co(III) gives 66 mol of butenes	233
Co(acac)$_2$–$(C_2H_5)_2AlOC_2H_5$–BuLi	benzene/cyclohexane, 700 psi, 75 °C	1-butene (2%), *trans*-2-butene (17.2%), *cis*-2-butene (5.9%) 1-hexene (6.5%) (gas phase), butenes (29.4%), 1-hexene (6.5%) (liquid phase)		234
Co(acac)$_2$–$(C_2H_5)_3Al$	toluene, 50 °C	1-butene, 2-butenes	Co/Al = 1:9, selectivity to 1-butene is 66.6%, conversion to butenes is 1.8%	235
Co(acac)$_2$–$AlCl(C_2H_5)_2$–PPh_3	toluene, 50 °C	1-butene, 2-butenes	Co/Al/PPh_3 = 1:9:3; selectivity to 1-butene is 16.8%; conversn to butenes is 39.7%	235
Co(acac)$_2$ supported on $Al_2(PO_4)_3$–$(CH_3)_3Al$	26 °C, 35 bar	1-butene, α-olefins	selectivity to 1-butene is 98% activity is 60 g/mol of Co.hr	236
R_pCo–R'_mAlX_{3-m}–phosphine (R = acyl or allyl or cyclopentadienyl, p = valency of metal, R' = alkyl, X = halogen)	*n*-heptane/benzene, –50 to +150 °C, 1.25 atm	butenes		105
$CoH(N_2)(PPh_3)_3$	25 °C	2-butenes (95–99%)		109
$CoX(PPh_3)_3$–$BF_3{\cdot}OEt_2$–$AlCl_3$/$SnCl_2$ (X = Cl^-, Br^-, I^-)	bromobenzene/iodobenzene/ *o*-dichlorobenzene/ chlorobenzene/	C_4^- distribution is 1-butene (90%), *trans*-2-butene (4.5%), *cis*-2-butene (5.5%)	order of reactivity is bromobenzene > iodobenzene > o-dichlorobenzene >	110, 111

	o-chlorotoluene		chlorobenzene > o-chlorotoluene, B–Co ratio is 1	
$CoBr_2(PPh_3)_2$–$(C_2H_5)AlCl_2$	toluene, 30 °C, 2 h	1-butene, 2-butene	1-butene/2-butene ratio = 1:20	237
$[Co(C_2H_4)(PPh_3)_3]_2$	benzene, 20 °C, 1 atm	*trans*-2-butene (63.0%), *cis*-2-butene (24.5%), 1-butene (1.5%), hexenes (10%)	E_a = 12.4 kcal/mol ΔH = 11.8 kcal/mol ΔS = 16 cal/(mol·K)	112
bochmite/bayerite/γ-Al_2O_3 impregnated with bis(*n*-butylsalicylideniminato)-cobalt(II)–$(C_2H_5)_3Al_2Cl_3$	chlorobenzene	butenes, hexenes, octenes		238
		Nickel		
(π-allyl)nickel halide–R_3Al		2-butenes (major), 1-butene		239, 240
(π-allyl)nickel halide–$TiCl_4$/$VOCl_3$	toluene, 8 atm, 55 °C, 3 h	1-butene (21%), *trans*-2-butene (52%), *cis*-2-butene (27%), hexenes, polymer (minor)		241, 242
(π-allyl)nickel complex–$AlCl_3$ alkylbenzene complex		butenes (major), hexenes, polymer		243
(π-allyl)nickel halide–$AlCl_3$/$AlBr_3$/$AlRCl_2$–PR_3		butenes		1, 118, 134, 143, 147, 148, 244, 245, 247
(π-allyl)nickel halide supported on Al_2O_3–$(C_2H_5)_3Al_2Cl_3$		1-butene, 2-butenes		159, 248
$(\pi\text{-}C_5H_5)_2Ni$	200 °C, 600 psi	2-butenes (major), 1-butene (minor)		2, 152, 153
$(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_7)Ni$	145–150 °C	1-butenes 82–90%	ethylene conversn is 70–90%	126
$(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_7)Ni$	benzene, 150 °C, 30 min	butenes (78%), hexene (15%), and octene (3%)	ethylene conversn is 90%	249
$(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_7)Ni$ supported on SiO_2–Al_2O_3	heptane, 50–75 °C, 1 h	butenes, hexenes, octenes	ethylene conversn is 84%	250
$(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_7)Ni$ supported on SiO_2–Al_2O_3	14–21 atm, 50–60 °C, 1 h	$C_4^=$ (47%), $C_6^=$ (27%), $C_8^=$ (9%), $C_{10}^=$ (7%), $C_{12}^=$–$C_{22}^=$ (10%)	1-butene in $C_4^=$ is 95%	251
$Ni(acac)_2$–$R_{6-x}Al_2Cl_x$–PPh_3 (x = 2, 3, or 4)		butenes	97.3% 1-butene at ethylene conversn of 4.1%; 95% 1-butene at ethylene conversn of 48%	125, 130, 252, 253, 254, 256, 257
$Ni(acac)_2$–$(C_2H_5)_3Al$–BCl_3	heptane, 20 min, 60 °C, 15 kg/cm^2	butenes		258
$Ni(acac)_2$–$(C_2H_5)_2AlCl$–PPh_3	toluene, 50 °C	1-butene, 2-butenes	[Ni]/[Al]/[PPh_3] = 1:9:3; amount of butenes is 48.6%; 1-butene in $C_4^=$ is 5%; 2-butene is 95%	235
$Ni(acac)_2$–$(C_2H_5)_3Al_2Cl_3$–PR_3 (R = Bu, Ph, PhO)		butenes	with phosphines 85.5–55.1% of butenes whereas with phosphites 77.2–95.8% butenes are formed	133, 136, 138, 156, 157
$Ni(acac)_2$–$(C_2H_5)_3Al$–$(C_2H_5O)_3Al$–$PhC{\equiv}CH$	xylene, 110 °C, 60 atm, 5 h	1-butene (86%)		259
$Ni(acac)_2$–$(C_2H_5)_3Al$	60–150 °C, 20–80 atm	1-butene, 1-hexene, 2-butene, 2-hexene	Al/cat. ratio is 0.45–4.2 for optimum yield of 1-butene	246
$Ni(acac)_2$ supported on brominated polystyrene–$BF_3{\cdot}OEt_2$/$(i\text{-}Bu)_3Al$		2-butenes (98%), 3-methylpentenes, 1-butene		119
$Ni(acac)_2$ supported on SiO_2–Al_2O_3 or Al_2O_3–$(C_2H_5)_2AlCl$–PPh_3		butenes		261, 262, 263
$Ni(acac)_2$ supported on inorganic oxide–$(CH_3)_3Al$	toluene, >1 atm, 65 °C	1-butene, 1-hexene, 2-butene, 2-, 3-hexenes	selectivity is 90%; cat. activity is 60 g/mmol of nickel/h	264
$Ni(acac)_2$ attached to Graft copolymer of (ethylene–propylene–dicyclopentadiene with 4-vinylpyridine)–$(i\text{-}C_4H_9)_3Al$		1-butene (37%), *cis*-2-butene (26%), *trans*-2-butene (37%)		265

TABLE II (Continued)

cat.	reactn condtn	products	comments	ref
Ni(acac)$_2$ supported on (ethylene–propylene–vinylnorbornene) copolymer–ClAl(i-C$_3$H$_7$)$_2$–PPh$_3$	20 °C, 2.5 atm	1-butene (80%), *cis*-2-butene (9%), *trans*-2-butene (11%)		266
nickel fluoroacetylacetonate–(C$_2$H$_5$)$_2$Al(OC$_2$H$_5$)		butenes		267
nickel salts–haloorganoaluminums–B(OR)$_3$	halohydrocarbons, −10 to 100 °C	2-butenes		268
NiCl$_2$–AlCl$_3$–PR$_3$/amine	chlorobenzene, 20 °C	butenes (78%), C$_6$ olefins (20%)		269, 270
NiCl$_2$ or Ni(OAc)$_2$–NaBH$_4$–phosphinobenzoic acid	HO(CH$_2$)$_4$OH	C$_4$ and higher olefins (8–34%)		271
NiCl$_2$·6H$_2$O–Ph$_2$PCH$_2$CO$_2$K–NaBH$_4$	HO(CH$_2$)$_4$OH, 75 °C, 750 psig	butenes (45%), C$_6$–C$_{10}$ olefins (48%), C$_{12}$–C$_{20}$ olefins (6.3%)	Ni/ligand = 1; NaBH$_4$/Ni = 2; activity = 2350 g/g of Ni/h	272
NiX$_2$–Ph$_2$PCH$_2$CO$_2$H–NaBH$_4$–PPh$_3$	HO(CH$_2$)$_4$OH, 100 °C, 40 atm	C$_4^=$–C$_8^=$ (41%), C$_{10}^=$–C$_{18}^=$ (40.5%), C$_{20}^=$ (18.5%)		273–275
polymeric gel immobilized NiCl$_2$/Ni(NO$_3$)$_2$–(C$_2$H$_5$)AlCl$_2$		butenes		276
trans-(PPh$_3$)$_2$Ni(σ-aryl)Br	chlorobenzene/CH$_2$Cl$_2$, 0 °C, 1 atm	butenes		117, 277
NiBr(L)(PPh$_3$)$_2$–BF$_3$·OEt$_2$ (I = Br, mesityl, naphthyl, o-tolyl)		butenes	rate of dimerization increases in the order Br << mesityl < naphthyl < o-tolyl	114, 120, 127
(C$_6$Cl$_5$)Ni(PPh$_3$)$_2$Cl–AgClO$_4$–PPh$_3$	bromobenzene, 0 °C, 1 atm	butenes	selectivity is 80–100%	152
(C$_6$H$_5$)Ni(PPh$_3$)$_2$Br–AgClO$_4$		butenes	max activity for AgClO$_4$/nickel complex = 2	154, 278
(o-tolyl)Ni(PPh$_3$)$_2$Br/(1-naphthyl)Ni(PPh$_3$)$_2$Br/(mesityl)Ni(PPh$_3$)$_2$Br–BF$_3$·OEt$_2$	CH$_2$Cl$_2$, 0 °C, 5 min	butenes		279
NiX$_2$(PR$_3$)$_2$–Al$_2$R$_{6-x}$Cl$_x$–haloalkane (x = 2, 3, or 4)		butenes	[Ni]/[Al] = 1:20–85; haloalkane/Al = 1–18:1	280, 281, 282
NiCl$_2$(PBu$_3$)$_2$–(C$_2$H$_5$)$_2$AlCl–C$_3$–C$_{12}$ alkyl halide		butenes		283
LNiPh$_3$P=CHBz		α-olefins		284
NiX$_2$–PR$_3$–R′$_n$AlX$_{3-n}$ supported on solid carrier (X = halogen, R = alkyl, cycloalkyl, R′ = R, n = 1, 3)		butenes		285
NiCl$_2$(PBu$_3$)$_2$ supported on SiO$_2$–Al$_2$O$_3$–(C$_2$H$_5$)$_2$AlCl	300 °F, 2 h	1-butene (12%), 2-butene (88%)	selectivity to butene is 68–73%	286
NiX$_2$–PR$_3$/pyridine/bipyridyl–RAlX$_2$ (R = alkyl)	chlorobenzene	butenes		287
NiX$_2$(PR$_3$)$_2$–Al$_2$R$_{6-x}$Cl$_x$ (x = 2, 3, or 4)		1-butene, 2-butenes, hexenes, 3-methylpentenes		150, 158
HNiCl[P(i-PrO)$_3$]–(C$_2$H$_5$)$_3$Al$_2$Cl$_3$		butenes		124
	toluene/chlorobenzene, 25 °C, 80 psi	cyclobutane (19.8%) and 1-butene (89.2%) in toluene medium whereas in chlorobenzene 99.4% butenes are formed	toluene favors cyclobutane and chlorobenzene favors 1-butene, but toluene with LiCl gives 1-butene	155
Ni(PPh$_3$)$_4$–AlCl$_3$/AlBr$_3$	chlorobenzene, 50 °C	1-butene (4.4%), *trans*-2-butene (68.5%), *cis*-2-butene (27%)		288
Ni(PPh$_3$)$_4$ supported on polymer, BF$_3$·OEt$_2$	hexane, 0 °C, 1 atm, toluene	butenes		121, 180, 289
polystyrene supported Ni(PPh$_3$)$_4$–BF$_3$·OEt$_2$–(C$_2$H$_5$)$_3$Al$_2$Cl$_3$–PPh$_3$		butenes, 3-methyl-pentenes		136, 156, 157
Ni(PCl$_3$)$_4$–AlBr$_3$–LiBu	chlorobenzene, argon, 1 atm, 20 °C, 30 min	1-butene and *cis*- and *trans*-2-butenes		116, 269, 290, 291

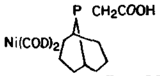
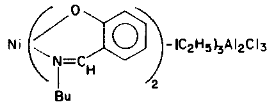
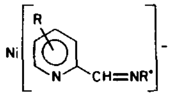
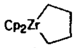
$Ni(PPh_3)_2(NO)_2$–$(C_2H_5)AlCl_2$		butenes, hexenes, octene		292
$Ni(CO)_4$–PPh_3–$(C_2H_5)_3Al_2Cl_3$ supported on Al_2O_3		C_4 hydrocarbons		293
$Ni(CO)_4$–$(C_2H_5)_2AlCl$–$(C_2H_5)AlCl_2$–PPh_3	benzene, 400 psi, 101 min, 252 °C	butane (0.1%), 1-butene (8.35%), 2-butene (30.38%), higher olefins (35.72%)		294
$Ni(CO)_x(PR_3)_{4-x}$–$Al_2R_{6-x}Cl_x$ ($x = 2$)		butenes		290
$Ni(CO)_2(PPh_3)_2$ supported on Al_2O_3–SiO_2–$(C_2H_5)_nAlCl_{3-n}$ ($n = 1, 2$)	aliphatic or aromatic hydrocarbon 20°–80° C, 2-20 atm	butenes	cat./activator mole ratio is 8.736:1	295, 296
$Ni(PR_3)_2$(ethylene)–$AlCl_3$		butenes		297
Ni(ethylene)$_3$–$BF_3{\cdot}OEt_2$–$AlCl_3$		butenes	maximum activity with BF_3/Ni mole ratio = 3 and $AlCl_3$/Ni mole ratio = 4	131
Ni(ethylene)$_2$(i-PPr_3)/Ni(ethylene)-(i-PPr_3)$_2$–$BF_3{\cdot}OEt_2$–$AlBr_3$		1-butene, *cis*- and *trans*-2-butene, 3-methyl-1-pentene, 3-methyl-2-pentene, *trans*-2- and *trans*-3-hexenes	butenes and hexenes are in the ratio 2:1	122, 123
(ethylene)$_2$Ni(i-PPr_3)–BF_3		butenes		129
NiL_2–$(C_2H_5)AlCl_2$ (L = picoline)	chlorobenzene, 80–100 psig, 180 °F, 12 min	butene (59%), hexene (35.7%), octene (6.9%)		292, 298
NiL_2–$(C_2H_5)_2AlCl$ (L = o-phenylenediamine)	10–30 °C, 5–20 atm	butenes		299
$NiCl_2$(3-picoline)$_2$ supported on SiO_2–Al_2O_3–$(C_2H_5)_2AlCl$		butenes		286
$Ni(S_2CNR_2)_2$–$(C_2H_5)AlCl_2$ (R = butyl)	chlorobenzene	butenes, hexenes, octene		292
Ni(π-L)$_2X_2$–$Al_2R_{6-x}Cl_x$–PR_3 (x = 2, 3, or 4) (L = tetramethylcyclobutadiene)	1 atm, 1 h, 20 °C	C_6 olefins (17%), 1-butene (78%)		150, 158, 295, 300–305
$Ni(COD)_2$–$CF_3COCH_2COCF_3$	toluene	butenes	mole ratio of cat. to additive is 0.5:1–2:1	306
$Ni(COD)_2$–CF_3CO_2H	toluene, 10 h, 25 °C, 500 psi	butenes, higher α-olefins	32 g of oligomers/g of cat./$h\nu$	307, 308
$Ni(COD)_2$–$Ph_2PCH_2CO_2H$	benzene, 75 °C, 550 psig, 4 h	higher olefins, C_4 to C_{22} olefins		309
$Ni(COD)_2$–PPh_2CH_2COOH	toluene, 25 °C, 50 bar	C_4–C_{24} olefins	linearity (99%), α-olefins (99%)	310, 311, 312
$Ni(COD)_2$–PPh_2CH_2COOH supported on Al_2O_3–SiO_2	50 °C, 20 bar, 3 s	C_4–C_{20} olefins	C_4 100% linear and 50–90% α-olefins, C_6–C_{20} 80% linear and 48% α-olefins	310
$Ni(COD)_2$–PPh_3–$Ph_3P{=}CHCOPh$	toluene, 50 °C, 50 bar	C_4–C_{30} olefins	linearity (99%) and α-olefins (98%)	284, 313
	aromatic solvents	α-olefins (99%)	activity is 6000 mol of ethylene/mol of complex	260, 314
NiX_2L_2–$Al_2R_{6-x}Cl_x$ (L = hexamethylphosphoramide, x = 2, 3, or 4)		butenes		315
$NiBr_2/NiCl_2$–phosphoric tris(diamide)–$AlR_3/AlRX_2$		butenes, hexenes		316
Ni oleate–(i-C_4H_9)$_2$AlCl–(t-Bu)C_6H_4Me/oxygen	*n*-heptane, 1 atm; 30 °C, argon	butenes, hexenes	Al/Ni ratio = 4:6	105, 317, 318
Ni oleate–$(C_2H_5)_3Al_2Cl_3$–PPh_3	*tert*-butyltoluene, 20 °C, 3 h	butenes (80%)	ethylene conversn is 48%; Ni/PPh_3 ratio = 1:2	319
Ni palmitate–$(C_2H_5)_3$Al–PhC≡CH	110–130 °C, 40 atm, 200 h	1-butene	selectivity is high	320, 321, 322
Ni diisopropylsalicylate–$Al_2R_{6-x}Cl_x$ (x = 2, 3, or 4)	isooctane, 1 h, 0/30 °C	1-butene (5.8/10.8%), *cis*-2-butene (20.3/20.1%), *trans*-2-butene (53.2/52.5%), hexenes (20.7/16.6%)		323
$Ni(RCO_2)_2$–R_mAlX_{3-m}–PX_3 (R = alkyl, aryl; m = 1, 2; X = halogen)	−50 °C to +150 °C, 25 atm	butenes		324, 325
bochmite/γ-Al_2O_3 impregnated with	chlorobenzene	butenes, hexenes, octenes		326

TABLE II (Continued)

cat.	reactn condtn	products	comments	ref
				
 group VIII metal halides (R = H, Me, Cl; R = $(CH_2)_2NR^2R^3$,R^2 = R^3 = H, alkyl)	0 °C, 20 min	butenes, hexenes		327
$Ni(Me_2SO)_6$·$NiCl_4$–$(C_2H_5)_3Al_2Cl_3$/ $(C_2H_5)AlCl_2$	ethyl chloride	butenes (61%), hexenes (36%), octenes (23%)		328
$CpNi(C_2H_4)(C_2H_5)$	120 °C	butenes, hexene, octene		329
		Copper		
$CuAlCl_4/Cu_2Cl_2/(C_2H_5)AlCl_2/$ $(C_2H_5)_2AlCl$		butenes		33, 34
		Zinc		
$ZnAl_2Cl_8$–$(C_2H_5)AlCl_2$		butenes		33, 34
		Zirconium		
$Zr(OR)_4$–$Al(C_2H_5)_3$ (R = Bu or C_2H_5)	diesel oil, 90 °C	1-butene (90%), hexenes (10%), octenes		209, 330
Zr(O-*i*-Pr)$_4$–$Al_2Cl_3(C_2H_5)_3$	heptane, 80 °C	C_4, C_6, C_8, and higher α-olefins	Zr/Al/P ratio = 1:10–25:1–3	88
Zr(O-*n*-Bu)$_2$(OC_6H_4Cl-4)$_2$–PPh_3–$(C_2H_5)_2AlCl$	toluene, 50 °C, 1 h 9 kg/cm^2	1-butene (58.4%), 1-hexene (29%), 1-octene (12.6%)	Zr/Al/P wt ratio = 8.3:46:1	331
$Zr(OR)_4$–R_xAlX_{3-x}–PBu_3	organic solvents	1-butene		87
(π-allyl)$ZrBr_3$/ $C_6H_5CH_2ZrBr_3$–$(C_2H_5)_2AlCl$/ $(C_2H_5)AlCl_2$		C_4 and higher olefins		332
L_2ZrH_3 (L = Me_2PCH_2–CH_2PMe_2)		butenes		89
	toluene, 60 °C, 1 atm	*n*-butane, 1-butene, ethane		90
Zr(benzyl)$_4$–$(C_2H_5)_3Al_2Cl_3$	toluene, 40–80 °C	α-olefins		20
(η-C_4H_6)$_2$Zr(dmpe) (C_4H_6 = 1,3-butadiene, dmpe = $Me_2PCH_2CH_2PMe_2$)		1-butene, 3-methyl-1-pentene, 2-methyl-1-propene		81
		Niobium		
L_2NbH_5 (L = $Me_2PCH_2CH_2PMe_2$)		butenes		89
$(C_6H_5)Nb(C_8H_8)_2$		butenes (72.1%)		93
		Molybdenum		
[(π-C_6H_6)Mo(π-L)Cl]$_2$–$(C_2H_5)AlCl_2$	benzene, 20 °C	butenes		102
		Ruthenium		
$RuCl_3$	methyl alcohol, 500–800 atm, 10 h, 130 °C	1-butene, 2-butenes, C_6, C_8, and higher olefins		160, 161
$Ru(CO)_2Cl_2$ bonded to SiO_2 or silica gel or Al_2O_3 through silane derivatives containing amino group		butenes		333

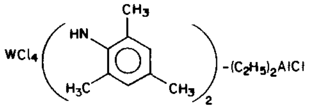
		Rhodium		
$RhCl_3 \cdot 3H_2O$–HCl	alcohol	1-butene, 2-butenes		160–163, 334, 335, 336
$RhCl_3 \cdot 3H_2O$	$CHCl_3$	1-butene, 2-butenes		171, 337
$RhCl_3$/$RhCl_3$ on SiO_2/$RhCl_3$ on SiO_2–Al_2O_3/$RhCl_3$ on Al_2O_3–HCl		1-butene, 2-butenes	the activity is SiO_2 supported cat. > SiO_2–Al_2O_3 supported cat. > Al_2O_3 supported cat.	165, 166
$RhCl_3$–$LiAlH_4$–PPh_3	benzene, 180 °C, 1050 bars, 1 h	1-butene, 2-butenes, C_{22} olefin		338
(π-C_5H_5)Rh(C_2H_4)$_2$		1-butene, 2-butenes		162
[Rh(CO)$_2$Cl]$_2$ bonded on SiO_2 or silica gel or Al_2O_3 or zeolite by use of silane derivatives	xylene	butenes		333
$Rh_2Cl_2(SnCl_3)_4$–HCl	ethanol/MeOH, 50–70 °C, 1.5–4 atm	butenes		339
$[Rh(SnCl_3)_2Cl_4]^{3-}$ anchored on AV 17-8 anion-exchange resin–HCl		*cis*-2-butene (88%), *trans*-2-butene		167, 340
		Palladium		
$PdCl_2$–HCl	$CHCl_3$/CH_2Cl_2–EtOH, 20–70 °C, 1–40 atm	2-butene (95–99%), 1-butene (1–5%)		168, 337
$PdCl_2$–HCl	CH_3COOH, 55 atm, 10 hr, 90 °C	2-butene (95–99%), 1-butene (1–5%)		336, 337, 341, 342
$PdCl_2$–RNO_2		2-butenes, 1-butene		170
$PdCl_2$–sulfones	benzene, 18 h, 75 °C, 750 psig	2-butenes, 1-butene	conversn of ethylene is 80%	343
$PdCl_2$–$CH_3CH(NO_2)CH_3$	1 atm, 40–50 °C, 5 h	butenes (96.7%), hexene (0.7%), nitropropane (1%)		344
$PdCl_2$	halogenated hydrocarbon/ RNO_2	2-butenes, 1-butene		168, 170–172
$PdCl_2$(ethylene)		butenes		337
Pd_2Cl_4(ethylene)$_2$	dioxane/benzene	butenes		169, 345
[(π-methylallyl)PdCl]$_2$–AgF_4–PBu_3		butenes, hexenes (≤25%)		346
polymer supported Pd(PPh_3)$_4$–$BF_3 \cdot OEt_2$	hexane	butenes		180
Pd(CN)$_2$/PdF_2/$PdBr_2$/PdI_2/Pd(NO_3)$_2$		butenes		6
Pd(BZCN)$_2$Cl$_2$	dibutylphthalate, benzene	butenes		173, 174
$PdCl_2$ supported on silica gel or Al_2O_3		butenes		176
$PdCl_2(Me_2SO)_2$/K^+[(Me_2SO)$PdCl_3$] supported on silica gel	90 °C	butenes		177–179
[(η-arene)$PdAl_mCl_n$]$_2$ (arene = C_6H_6, toluene; m = 1; n = 4)	25 °C	butenes	85–95% dimerization has taken place	175
		Silver		
$AgCl_4$–$(C_2H_5)_2AlCl$/$(C_2H_5)AlCl_2$		butenes		33, 34
		Hafnium		
L_2HfH_3 (L = $(CH_3)_2PCH_2CH_2P(CH_3)_2$)		butenes		89
		Tantalum		
L_2TaH_5 (L = dmpe)		butenes		89
$CpTaCl_2(C_4H_8)$ (Cp = cyclopentadienyl anion; C_4H_8 = butadiene)	40 psig	1-butene with 2-butenes (~3%)		347, 348
$(CH_2CMe_3)_3Ta(CHCMe_3)_3$–$PMe_3$	pentane, 25 °C	1-butene		9, 94, 95, 97, 98
		Tungsten		
	benzene, 40 °C	butene (98%)	conversn 84 000 mol/mol of tungsten/h	349

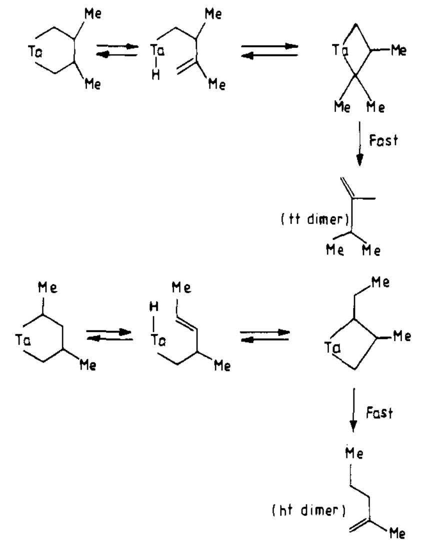
TABLE II (Continued)

cat.	reactn condtn	products	comments	ref
$WCl_6-(C_2H_5)_2AlCl-2,6-(CH_3)_2-C_6H_3NH_2$	chlorobenzene, 1 h, 40 °C, 27 atm	1-butene (92%)		103
		Iridium		
$IrCl_3$	ethyl alcohol	2-butene (95–99%), 1-butene (1–5%)		161
		Platinum		
$Pt(PPh_3)_4$ supported on polymer–BF_3-OEt_2	hexane	butenes		180

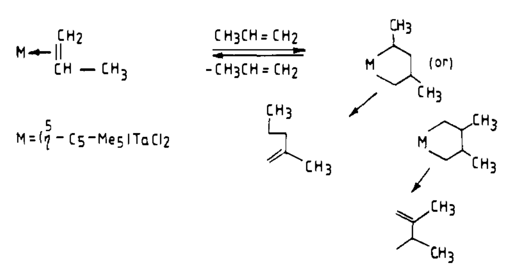
TABLE III. Representative Kinetic Data for the Dimerization of Ethylene

cat. system	reactn conditions	rate data, (T, °C)	remarks	ref
$Al(C_2H_5)_3$	416.7 torr	1.038×10^{-2} $mol^{-1}\cdot L\cdot s^{-1}$ (167)	rate constants at other temp. and pressures given	35
$Al(C_2H_5)_3$	*n*-decane, 9–120 psi	0.10 $mol^{-1}\cdot L\cdot min^{-1}$ (100)	E_a = 15 kcal/mol	52
$Ti(n\text{-}C_4H_9O)_4-AlR_3$ (R = CH_3, C_2H_5, $n\text{-}C_4H_9$)	diethyl or dibutyl ether	20 g/(L·min) (60)		67
$Ti(n\text{-}C_4H_9O)_4-Al(C_2H_5)_3$	pentane–dioxan, 1.5 MP_a	4.17 g/(L·min) (50)		197
$Ti(i\text{-}C_3H_7O)_4-Al(C_2H_5)_3$	heptane, 7.12 atm, Al/M = 5.6	1.3 g/(L·min) (90)		47
$Ti(acac)_2Cl_2-Al(C_2H_5)_3$	heptane, 7.12 atm, Al/M = 4.9	0.18 g/(L·min) (90)		47
$Ti(acac)_2(OC_2H_5)_2-Al(C_2H_5)_3$	heptane, 7.12 atm, Al/M = 6.1	0.08 g/(L·min) (90)		47
$Ti(OC_6H_4CH_3)_4-Al(C_2H_5)_3$	heptane, 7.12 atm, Al/M = 3.7	1.3 g/(L·min) (90)		47
$Ti(OC_6H_5)_4-Al(C_2H_5)_3$	heptane, 15 kg/(cm^2·g), Al/Ti = 3.0	0.5 g/min (40)		58
$Ti(OC_6H_4CH_3)_4-Al(C_2H_5)_3$	heptane, 15 kg/(cm^2·g), Al/Ti = 3.0	0.5 g/min (40)		58
$Ti(OC_6H_4Am)_4-Al(C_2H_5)_3-P(OPr)_3$	heptane, 15 kg/(cm^2·g), P/Ti = 4.0	1.31 g/min (60)		58
$Ti(OC_4H_9)-Al\text{-}i\text{-}Bu_3$	decane, 1 bar, Al/Ti = 4.5	1.125 g/(L·min) (20)		64
$Ti(OC_4H_9)_4-Al(C_2H_5)_3$	heptane, 4 atm, Al/Ti = 10	0.243 g/min (20)	rates in other solvents given	62
$Ti(OC_4H_9)_4-Al(C_2H_5)_3$	heptane, 10 atm, Al–Ti = 7.5	0.25 g/min (20)		62
$Ti(OC_4H_9)_4-Al(CH_3)_3$	heptane, 10 atm, Al/Ti = 7.5	0.18 g/min (20)		62
$Ti(OC_4H_9)_4-Al(i\text{-}Pr)_3$	heptane, 10 atm, Al/Ti = 7.5	0.09 g/min (20)		62
$Ti(O\text{-}n\text{-}C_4H_9)_4-Al(C_2H_5)_3$	toluene, 10 atm, Al/Ti = 10	0.77 g/min (20)	rates for other alkoxides given	62
$Ti(OC_4H_9)_4-Al(C_2H_5)_3$	heptane, 460 torr, Al/Ti = 10	3.5 g/(L·min) (22)		63
$Ti(OC_2H_5)_4-Al(C_2H_5)_3$	*n*-decane, 2.7 atm, 2 h	1.83 g/(L·min) (20)		222
$Ti(OC_4H_9)_4-Al(C_2H_5)_3-$*m*-phenylenediamine	*n*-heptane, 3 atm, 280 min	1.57 g/(L·min) (20)		222
$Ti(OC_4H_9)_4-Al(i\text{-}Bu)_2H$	diethyl ether, 9.3 atm, 109 min	6.5 g/(L·min) (60)		222
WCl_6–2,6-dimethylaniline–$(C_2H_5)_2AlCl$	benzene, 1 h, 27 atm	0.85 mol/(L·min) (40)		349
$[Co(C_2H_4)(PPh_3)_3]_2$	benzene, 1 atm	6.59 $mol^{-1}\cdot L\cdot min^{-1}$ (10)		112
$Ni(C_6H_5)Br(PPh_3)_2-BF_3\text{-}OEt_2$	CH_2Cl_2, 1 atm	0.05 g/min (0)		289
$V(O\text{-}C_3H_7)_4-Al(C_2H_5)_3$	Al/M = 3.8, 7.12 atm	0.17 g/(L·min) (90)		47
$CrCl_2(NO)_2(Ph_3PO)_2-(C_2H_5)AlCl_2$	chlorobenzene, 500 psig, 1 h	7.6 g/(L·min) (50)		99
$CrCl_2(4\text{-}Etpy)_2-(C_2H_5)AlCl_2$	chlorobenzene, 500 psig, 1 h	7.5 g/(L·min) (50)		99
$CrCl_2(NO)_2(4\text{-}Etpy)_2-(C_2H_5)AlCl_2$	chlorobenzene, 500 psig 1 h	7.9 g/(L·min) (50)		99
$CrCl_3(py)_3-(C_2H_5)AlCl_2$	chlorobenzene, 750 psig 1 h, Al/Cr = 5	6.8 g/(L·min) (50)		99
$CrCl_3(Bu_3P)_2-(C_2H_5)AlCl_2$	chlorobenzene, 500 psig, 1 h, Al/Cr = 5	7.5 g/(L·min) (50)		99
$RhCl_3\cdot 3H_2O$	EtOH–HCl, 4 atm	3.2×10^{-4} g/min (33)	E_a = 13.6 kcal/mol	33
$[RhCl(C_2H_4)_2]_2$	EtOH–HCl, 4 atm	1.01×10^{-4} g/min (20)	E_a = 14.7 kcal/mol	163

SCHEME XXIII. Formation of ht and tt Propylene Dimers from Tantalacyclopentane Complexes



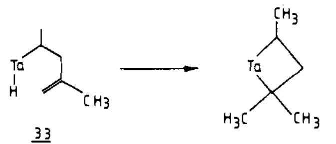
lective catalytic dimerization of propylene to a mixture of tail to tail (tt) and head to tail (ht) dimers[94] (eq 17).



(17)

The investigators of the above work have also observed that $(\eta^5\text{-}C_5H_5)Cl_2\underline{TaCH_2CHMeCHMeCH_2}$ is the crucial intermediate in the catalytic dimerization of propylene to largely 2,3-dimethyl-1-butene. Unfortunately this catalyst system becomes inactive after ~20 turnovers, possibly because $Ta(\eta^5\text{-}C_5H_5)Cl_2(C_3H_6)$ which must be formed as intermediate is unstable at 25 °C.[378]

Deuterium labeling studies show that each tantalacyclopentane ring contracts to the tt or ht dimer.[95] An alkenyl hydride complex is an intermediate in each pathway (Scheme XXIII). It forms reversibly from the tantalacyclopentane complex. The rate of the ring contraction step may be kinetically important, and decomposition of the tantalacyclopentane complex is fast relative to the rate at which it forms its alkenyl hydride precursor. In the second pathway the β-hydrogen abstraction can lead to **33** and subsequently to an α,α,α′-trisubstituted metallacycle (eq 18).



33

(18)

This is much more sterically crowded than the α,β-disubstituted metallacycle given in the original pathway. This choice is applicable only to α,β′-disubstituted metallacyclopentane rings since the β,β-disubstituted metallacyclopentane must collapse to the much more crowded α,α,β-trimethyltantalacyclopentane complex.

F. Group 6 (VIB) Elements

1. Chromium

$CrCl_3(py)_3$, $CrCl_3(4\text{-}Etpy)_3$, and $[CrCl_3(PBu_3)_2]_2$ complexes have been used as catalysts[94,101] for the dimerization of propylene. In addition to dimers, trimers and tetramers are formed. The C_6 fraction is composed mainly of 2-methylpentene (69%) and n-hexenes (31%). $EtAlCl_2$ is used as the cocatalyst in these systems.

2. Tungsten

Treatment of WCl_6 with aniline (ligand) and $Et_3Al_2Cl_3$ gives $HWCl_3{\cdot}H_2NPh$ which on reaction with propylene is converted into a series of reaction intermediates.[379,380] The order in which the reagents are combined is important to the reaction. As the Al/W ratio decreases, the proportion of dimerization also decreases. WCl_6 or WBr_5 heated at 132 °C with aniline in conjugation with $EtAlCl_2$ is also used as a catalyst for the dimerization of propylene at 60 °C.[207] Conversion of propylene is 39%, and selectivity for C_6 olefins is 98% with this method.

Additives like phenols,[381] carboxylic acid esters,[382] and diketones[383] with the $WCl_3\text{–}PhNH_2\text{–}Et_3Al_2Cl_3$ system influence the conversion and selectivity of dimerization of propylene considerably. 2,3-Dimethyl-1-butene and 2-methyl-1-pentene are the major products in all these reactions. A WCl_6/additive mole ratio of 1:1 is employed. The $WCl_6\text{–}OHC_6H_4COOCH_3$[381] system gives 94% conversion and 99% selectivity to hexenes. On the other hand, the $WCl_6\text{–}C_6H_5CH_2OH$ system produces 77% conversion and 90% selectivity to dimers.[382]

G. Group 7 (VIIB) Elements

There is a patent report[384] on a manganese-based metal complex as a catalyst for the dimerization of propylene. When $AlCl_3$ is added to $MnCl_2$, it forms a 1:1 complex initially. Here $AlCl_3$ acts as a Lewis acid. If $AlPr_3$ and propylene are added to this, 2- and 4-methyl-2-pentenes and 2-hexenes are formed. Activity of the catalyst increases with an increase in complex concentration.

H. Group 8–10 (VIII) Elements

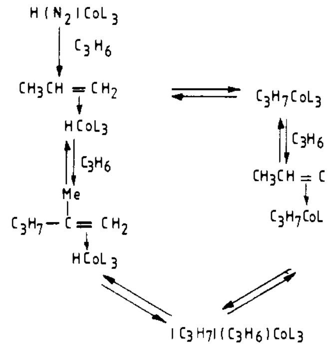
1. Iron

The $FeCl_3\text{–}AlCl_3$ (1:1) system with $AlPr_3$ cocatalyst is a good catalyst for propylene dimerization. It has higher activity than the $MnCl_2\text{–}AlCl_3\text{–}AlPr_3$ system.[384] The $Fe(acac)_2\text{–}(i\text{-}Bu)_2AlCl$ system is also known to catalyze the dimerization of propylene.[385] The dimerization of propylene to 2-methyl-2-pentene in heptane, toluene, or chloroform solvents in the presence of the tricomponent system $Fe(acac)_n$ (where n = 2, 3)–Et_2AlCl–1,5-cyclooctadiene has also been patented.[386]

2. Cobalt

The two-component cobalt catalyst such as $CoCl_2\text{–}Et_2AlCl$ with methylene chloride has high activity for propylene dimerization. The following types of catalyst

SCHEME XXIV. $H(N_2)CoL_3$ (Where L = Tertiary Phosphine) Catalyzed Dimerization of Propylene



systems have also been used:[387] CoX_2–AlR_3; CoX_2–AlX_3 and related systems; CoX_2–AlX_3–AlR_3 (R = alkyl; X = halogen). Many of these systems have very high activities. The transition-metal salts give >95% selectivity to dimerization in some cases. The dimer products are similar in all cases and consist of 30% hexenes and 70% methylpentenes. Selectivity to *n*-hexenes is increased to 50% at 150 °C. It is presumed that cationic catalysis is involved.

The $CoCl_2$–$AlCl_3$ (1:1) complex system with $AlPr_3$ is effective for homogeneous dimerization of propylene. It has higher activity compared to the $MnCl_2$–$AlCl_3$–$AlPr_3$ and $FeCl_3$–$AlCl_3$–$AlPr_3$ systems.[384]

$HCo(N_2)(PPh_3)_3$ has been used to dimerize propylene.[109] 2-Methyl-1-pentene is the main product. The addition of 3 mol of tri-*n*-butylphosphine/mol of cobalt complex considerably reduced the dimerization rate. A mechanism as shown in Scheme XXIV is proposed.

The kinetics of homogeneous propylene dimerization with $HCo(N_2)(PPh_3)_3$[388] or $Co(N_2)(PPh_3)_3$[389] as catalysts under mild conditions can be described by eq 19, where

$$\text{Rate} = \frac{k_3K_1K_2[Co][C_3H_6)}{[PPh_3] + K_1 + K_1K_2[C_3H_6]} \qquad (19)$$

K_3, K_1, and K_2 are all constants. The following activation parameters are reported for the dimerization reaction: $\Delta E_a = 22.9$ kcal·mol^{-1}, $\Delta H^{\ddagger} = 22.3$ kcal·mol^{-1}, and $\Delta S^{\ddagger} = 13$ cal·mol^{-1}·K^{-1}. The $Co(acac)_2$–$(i\text{-}Bu)_2AlCl$ system catalyzes the dimerization of propylene to give methyl-substituted pentenes.[385]

3. Nickel

The predominant literature[132,390–394] on the propylene dimerization is based on the nature of the activity of complex organometallic catalysts based on nickel compounds and the effects of ligand attached to the nickel on the selectivity of the process.

The IFP Dimersol process (Dimersol G) for the single-stage dimerization of propylene yields hexenes present in high octane gasoline.[395,396] The process takes place under rigorously controlled conditions at reduced pressures and ambient temperature in the presence of catalytic amounts of a nickel and aluminum alkyl complex which is immediately destroyed in an NH_3–H_2O system on completion of the dimerization.

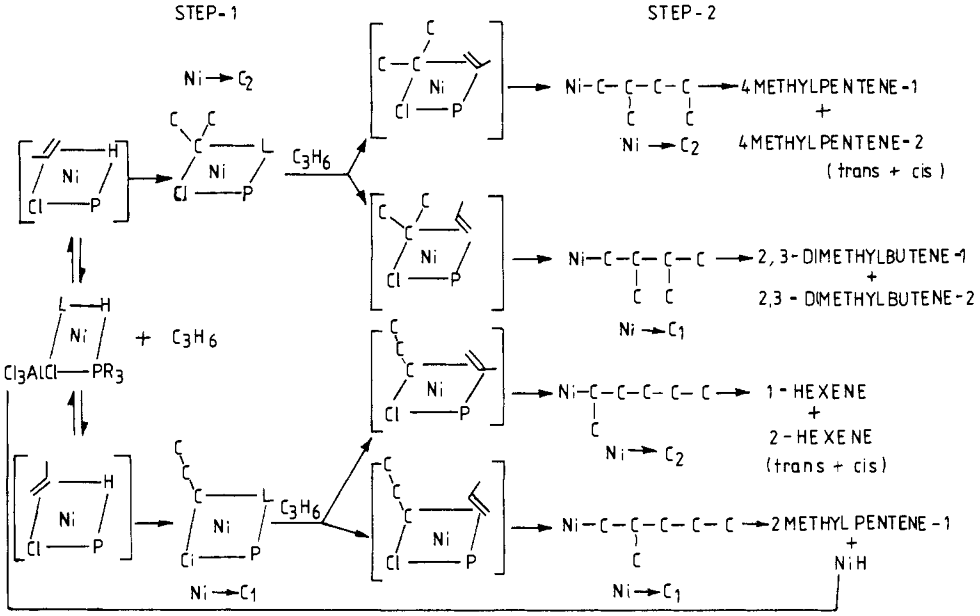
Catalysts based on (π-allyl)nickel halide are reported[143,244] to be used for the dimerization of propylene on a laboratory scale as well as pilot plant scale at the Max Planck Institute, West Germany. (π-Allyl)nickel halides with various cocatalysts like $AlCl_3$,[1,30,107,149,246] $TiCl_4$, $MoCl_5$, $VOCl_4$, and WCl_3[30,107,149,246] are active for the formation of *n*-hexenes, 2-methylpentenes, and 2,3-dimethylbutenes from propylene. When these catalysts are modified by adding tertiary phosphines, the dimerization of propylene can be diverted depending on the phosphines used[1,143] to give either 2-methylpentenes or 2,3-dimethylbutenes. These products are precursors of isoprene and 2,3-dimethylbutadiene, respectively. The mixture of them can be used as motor fuel constituents. The Lurgi-Ruhrgas Co. has set up an industrial plant for the dimerization of propylene having a capacity of about 100 000 ton/year.[244]

It has been suggested that the activity of complex Ziegler catalysts toward the dimerization of alkenes[107] arises from the formation of complex hydrides, for example, HNiCl, coordinated to the alkylaluminum halide. The study of the influence of phosphines on propylene dimerization has been studied extensively.[149,397–400] In the series of PPh_3 to $P(i\text{-}Pr)_3$ the yield of *n*-hexenes decreases gradually from 21.6 to 1.8% according to the order $PPh_3 > Ph_2P(CH_2)_3PPh_2 > Ph_2PCH_2Ph > Ph_2P(i\text{-}Pr) > Ph_2PCH_2PPh_2 > PMe_3 > PEt_3 > P(n\text{-}Bu)_3 > P(CH_2Ph)_3 > P(NEt_2)_3 > Cy_2PPCy_2 > PCY_3 > P(i\text{-}Pr^i)_3$. However, the yield of 2,3-dimethylbutenes increases up to 67.9% in the above series. Still higher yields of 2,3-dimethylbutenes are achieved by using phosphines with *tert*-butyl groups. However, with the introduction of two *tert*-butyl groups in combination with one isopropyl group in the phosphine the yield of 2,3-dimethylbutenes drops to 29.1%. There are two effects operating, namely, inductive effect of the group "R" attached to the phosphorous and the steric hindrance of the bulky *tert*-butyl groups. Better insight into the nature of the effect of phosphines on the catalytic reaction can be obtained when the mechanism and composition of dimers are taken into account.

The possible routes leading to the formation of different dimers are shown in Scheme XXV. A square-planar nickel hydride complex[401] is suggested as the catalytic species. In the first step the nickel hydride catalyst adds across the double bond of propylene to give two intermediates, namely, a propyl nickel and an isopropyl nickel complex. Both of these intermediates can react further with propylene by insertion of the double bond into the nickel–carbon bond resulting in formation of four more intermediates. β-Elimination of nickel hydride from these intermediates produces the possible products of propylene dimerization, namely, 4-methyl-1-pentene, *cis*- and *trans*-4-methyl-2-pentene, 2,3-dimethyl-1-butene, *n*-hexene, 2-hexenes, and 2-methyl-1-pentene. Terminal unbranched olefins are rapidly isomerized under the influence of catalyst by a process of repeated nickel hydride addition and elimination to the internal olefins. Therefore under ordinary reaction conditions the yield of 4-methyl-1-pentene is low.

The influence of phosphines on the direction of addition of nickel hydride or nickel alkyl to propylene is debatable. If it is assumed that the isopropyl nickel complex and the propyl nickel complex have the same reactivity toward propylene, the direction of addition

SCHEME XXV. Possible Routes Leading to Different Propylene Dimers in Presence of Nickel Complex



in the first reaction step (%) in the scheme is given by the ratio

$$\frac{\mathrm{Ni} \rightarrow \mathrm{C}_2}{\mathrm{Ni} \rightarrow \mathrm{C}_1} = \%\ (\text{4-methyl-1-pentene} + \text{4-methyl-2-pentene} + \text{2,3-dimethyl-1-butene} + \text{2,3-dimethyl-2-butene})/\{\%\ (\text{hexenes} + \text{2-methyl-1-pentene})\}$$

Similarly the average direction of addition in the second step is given by the ratio

$$\frac{\mathrm{Ni} \rightarrow \mathrm{C}_2}{\mathrm{Ni} \rightarrow \mathrm{C}_1} = \%\ (\text{4-methyl-1-pentene} + \text{4-methyl-2-pentene} + \text{hexenes})/\{\%\ (\text{2,3-dimethyl-1-butene} + \text{2,3-dimethyl-2-butene} + \text{2-methyl-1-pentene})\}$$

To obtain these ratios for different phosphines, it is necessary to avoid the isomerization of 2-methyl-1-pentene and 4-methyl-2-pentene. With strongly basic phosphines, the rate of isomerization as well as dimerization decreases in the order $PMe_3 > PPh_3 > PEt_3 > PCy_3 > (i\text{-Pr})P(t\text{-Bu})_2$. The isomerization can be suppressed at low conversion.

The amount of higher oligomers formed during the dimerization of propylene is also influenced by the nature of the phosphines. Their yield increases with the basicity of phosphines. Also the propylene dimers obtained with basic phosphines are isomerized only to a slight extent.

The dimerization of propylene on a $(\pi\text{-}C_3H_5)NiBr(PCy_3)$[402] in the presence of $EtAlCl_2$ proceeds with a turnover number of 60 at −75 °C and 230 at −55 °C. Extrapolated to 25 °C this gives a turnover number of 60 000 which is comparable to the activity of catalase. At higher conversions the catalyst has diminished activity. The product formed include 10–15% higher olefins, 18% 4-methyl-1-pentene, 1–3% *cis*-4-methyl-2-pentene, 76% 2,3-dimethyl-1-butene, and 4% 2-methyl-1-pentene as well as traces of other isomers.

With the $[\pi\text{-crotyl})NiCl]_2$–$TiCl_4$ catalyst system the activation energy for the dimerization of propylene is observed to be 15.2 kcal/mol.[403] The kinetics and product distribution for this and several other (π-allyl)nickel catalysts have been determined with PPh_3 as a proton acceptor: the yield of 2-methyl-2-pentene varies from ~13% to 56.5%.

There are reports[404–406] on the dimerization of propylene catalyzed by heterogenized (π-allyl)nickel halides. Polymer-anchored π-allylic nickel complexes similar to nonsupported complexes are found to be effective catalysts for propylene dimerization after activation with a Lewis acid such as $EtAlCl_2$ (molar ratio of Al/Ni = 15.5). Using a cross-linked resin as a support the dimerization can be performed continuously since the catalytic centers remain active for a long time without any further addition of aluminum cocatalyst. The release of metals during this reaction is low. The reactions are carried out either in bulk propylene or in chlorobenzene solution. The conversion reaches 95% at room temperature. The product has the composition of 2% dimethylbutenes, 67% methylpentenes, and 31% hexenes. Hexene content obtained with polymer-anchored nickel catalysts is higher than those observed with the (π-allyl)nickel triphenylphosphine complex with $EtAlCl_2$. The drawback of the polymer-anchored catalyst is that it loses 40% of its initial metal content after the reaction.

$Ni(acac)_2$–$Et_2Al(OEt)$[407] at 40 °C dimerizes propylene selectively to linear olefins, preferred solvents being ethers like diglyme. The optimum Al/Ni ratio is found to vary with different aluminum alkyls like $AlEt_3$, $Et_2Al(OEt)$, and $EtAl(OEt)_2$. With $AlMe_3$ and $Me_2Al(OEt)$ the optimum activity is observed at Al/Ni = 2:1. Maximum productivity is achieved between 20 and 40 °C. Investigation of the reaction with various β-diketones reveals that the nickel complex of dibenzoylmethane shows an improvement over nickel acetylacetonate on a molar basis. For this complex the optimum Al/Ni ratio is 1:1 for the $AlMe_3$ cocatalyst. Linear dimerization activity is also observed with alkyl compounds of lithium, boron, and magnesium. Of these the highest activity is observed by using BEt_3.

$Ni(acac)_2(i\text{-Bu})_2AlCl$ is reported to catalyze the dimerization of propylene to yield a mixture of dimers.

The dimer yield per unit weight of $Ni(acac)_2$ is improved by a factor of 5–8 when the homogeneous catalyst is replaced by $Ni(acac)_2$ on a solid carrier like Al_2O_3, SiO_2, or K_2CO_3. The catalytic activity of $Ni(acac)_2$ with Et_2AlCl, $Et_3Al_2Cl_3$, $EtAlBr_2$, and $EtAlCl_2$ are also observed.[385]

Thermodynamic constants have been calculated for 12 dimerization reactions of propylene at 5, 25, 127, and 227 °C, and the equilibrium composition[408] of the dimerization products at these temperatures has been determined. The influence of various phosphine additives in the $Ni(acac)_2$–$(i\text{-}Bu)_2AlCl$ catalyst system on the composition of dimerization products has been investigated and a dimerization scheme presented.

The same reaction is studied[409] in the presence of gel like catalytic systems (GCS) containing $Ni(acac)_2$ and $RAlX_2$. The activity of GCS in heptane, 2,2,4-trimethylpentane, and propylene dimers remains constant for hundreds of hours.

The activity of nickel salts supported on Al_2O_3 or SiO_2 in combination with the $(i\text{-}Bu)_2AlCl$ cocatalyst toward propylene dimerization decreases in the order[410] $Ni(acac)_2 > NiCl_2 > NiBr_2 > Ni(NO_3)_2 > NiSO_4$.

In the dimerization of propylene with a 1:45:16 Ni/Al/P mole ratio for the $Ni(acac)_2$–$Et_3Al_2Cl_3$–PPh_3 system raising the reaction temperature from −50 to 40 °C decreases the yield of 2-methylpentenes.[411] The yield of 2,3-dimethylbutenes increases, and the yield of hexenes remains constant. An increase in the P/Ni ratio from 0 to 8 at Al/Ni ratio of 45 is associated with decrease of hexenes and increase of 2,3-dimethylbutenes.

The effect of reaction parameters like catalyst concentration, temperature, and pressure on the selectivity of the dimerization of propylene in the presence of the catalytic system $Ni(acac)_2$–$(i\text{-}Bu)_2AlCl$–L (L = PPh_3, PCy_3, or $(Me_3C)_2PBr$) has been studied.[412] The isomerizing activity of phosphorous ligands is PPh_3 > catalyst without L > PCy_3 > $(Me_3C)_2PBr$. An increase in the pressure decreases the isomerization and increases the dimer yield. Optimum dimer yield is obtained at temperature from −10 to 20 °C. At low catalyst concentration in the presence of $(Me_3C)_2PBr$ 23% of thermodynamically unstable 4-methyl-1-pentene is obtained. Compounds like $P(OR)_3$ are recommended as modifiers for the above system in place of PPh_3.[413]

The nature of the phosphorus ligand in the $Ni(acac)_2$–$Et_3Al_2Cl_3$–PR_3 catalyst[142,401] on the dimerization of propylene in toluene is studied. The electronic effect of substituents in triarylphosphine $P(PhX)_3$ (X = p-Cl, p-H, p-Me, p-OMe, o-Me, etc.) on dimer distribution is measured. The catalytic activity decreases in the series p-Cl > p-H > o-Me ≈ p-Me > p-AC > p-Et > p-Bu. Both the basicity and molecular bulkiness of the phosphines favor formation of 2,3-dimethylbutenes rather than hexenes or 2-methylpentenes.

Propylene dimerization in toluene over a 1:8:3 $Ni(acac)_2$–PPh_3–$Et_3Al_2Cl_3$ catalyst[393,414] is second order in propylene and second order in catalyst. The thermodynamic parameters have been calculated for the catalyzed and uncatalyzed gas-phase reactions. The above catalyst system shows higher activity[415] at 10 °C than at 26 °C in the isomerization of 2-methyl-1-pentene. This suggests that the catalytic species is thermally unstable even at 26 °C. Very low temperatures of −50 to −20 °C have been employed to prevent deactivation of the catalyst. The kinetics of the dimerization is carried out in a static system containing propylene of comparatively high concentrations (propylene/Ni molar ratio = 240–2400). The rate law is given by

$$\frac{d[C_6H_{12}]}{dt} = k[Ni][C_3H_6]$$

$$k = 10^{10.1}e^{(-13000/RT)}\text{mol}^{-1}\cdot\text{l}\cdot\text{s}^{-1}$$

The rate law is different from that given by Hojabri,[393,414] based on data at high temperatures. This is because of the measurement of the rate by an integral method without taking into account the deactivation of the catalyst. Activation parameters have been evaluated as $E_a = 13.0$ kcal/mol, $k = 7.98 \times 10^{-3}$ mol^{-1}, L·s^{-1} at −40 °C, $\Delta H^{\ddagger} = 12.5$ kcal/mol at −40 °C (8.95), $\Delta S^{\ddagger} = -13.8$ cal·mol^{-1}·k^{-1} at −40 °C (0). The values in the parentheses are obtained by Hojabari at 30 °C. Insertion of propylene into the propyl nickel complex is taken to be the rate-determining step of the mechanism proposed.

The structure and yield of the propylene dimerization products have been studied as a function of the catalyst composition and solvent.[416] The highest yield is obtained in toluene with a relative molar composition of $Ni(acac)_2$–$AlEt_3$–PPh_3–$BF_3{\cdot}OEt_2$ as 2:1:4:35. It corresponds to the B/Ni molar ratio of 15. At a B/Ni molar ratio of <5 the system is catalytically inactive. When $BF_3{\cdot}OEt_2$ is preconditioned in anhydrous toluene for a few days, then the optimal ratio decreases. At the optimum catalyst composition the yield is the highest in toluene, then in benzene, and much lower in chlorobenzene, yet the relative distribution of products in toluene and chlorobenzene is closer than that in benzene. The Brønsted acid activates the catalyst containing nickel(0).

Complexes of $Ni(acac)_2(COD)$ and $Ni(acac)_2(C_4H_8)$ supported on polystyrene containing PEt_2, $P(i\text{-}Bu)_2$, $P(OEt)_2$, $P(NEt_2)_2$, and PCl_2. $AlCl_3$ along with Et_2AlCl, $EtAlCl_2$, or $(i\text{-}Bu)_2AlCl$ activators catalyze the dimerization of propylene giving 1300–1700 g of dimers/h/g of nickel.[417] The catalysts are stable for >1000 h in alkane solvent. The precise dimer composition depends on the catalyst components, solvent, and temperature.

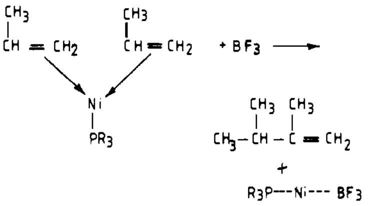
Nickel oleate with $Al_2R_{6-x}Cl_x$ (x = 2, 3, or 4) brings about the dimerization of propylene.[107,145,146] $Ni(O_2CC_{15}H_{31})_2$–Bu_2AlCl–L (L = dibenzo-18-crown-6, polyethylene glycol 2000, $X(CH_2CH_2O)_2CH_2CH_2X$ where X = piperidino, PhS, or PhO) containing a 50:1 ratio of Al/Ni catalyzes the reaction at 0–10 °C and 1 atm. Using crown ethers and polyethylene glycol ligands with the complex, ≤90% selectivity for methylpentenes can be achieved.[418]

$Ni(O_2CR)_2$ (R is undefined)–$(i\text{-}Bu)_2$ AlCl–piperidine or –morpholine systems are also known to dimerize propylene. Conversion of propylene is the highest (80–85%) with piperidine as the additive.[419]

Study of the dimerization of propylene in the presence of phosphine complexes of nickel(0) is available.[420,421] The $Ni(PPh_3)_4$–$AlBr_3$ or –$AlCl_3$, $Ni(PPh_3)_4$–$BF_3{\cdot}OEt_2$,[422,423] and $Ni(PPh_3)_4$–Et_2AlCl or –$Et_3Al_2Cl_3$[424] systems are a few of them. Addition of HF to a $Ni(PPh_3)_4$–BF_3 catalyst system for propylene dimerization up to a Ni/HF ratio of 1:1 significantly increases the rate. Analogous results[425] have been obtained upon the addition of HF and H_2SO_4 into the $Ni(PPh_3)_4$–$BF_3{\cdot}OEt_2$ catalytic system. The composition of the propylene dimers is hardly affected by the introduction of Bronsted acid into the catalytic system. The order of addition of these acids has a significant effect on the yield of hexenes. If HF is added to the $Ni(PPh_3)_4$ solution before the Lewis acid, the yield of hexenes is doubled. There is also a report on the dimerization of propylene catalyzed by $Ni(PPh_3)_4$ in conjunction with CF_3CO_2H.[426,427]

A polystyrylnickel complex prepared by the oxidative addition[345,428] of brominated polystyrene to $Ni(PPh_3)_4$ and activated with $BF_3{\cdot}OEt_2$ and a catalytic amount of water acts as an efficient catalyst for the dimerization of propylene at room temperature and atmospheric pressure. Solvents like *n*-hexane, toluene, benzene, methylene chloride, and chlorobenzene increase the rate of reaction. One role of the solvent is to swell the matrix polymer to allow access of the substrate olefin to the interior of the polymer gel. Some dipole–dipole interaction between the nickel site, the olefin, and the solvent molecule may be prevailing so that competitive coordination of the olefin and the solvent to the nickel site may be possible. The effect of temperature shows that the rate of the dimerization reaction decreases with an increase in temperature while selective formation of methylpentenes increases up to 90% at 40 °C. 2-Methyl-2-pentene is the major C_6 olefinic product.

$Ni(PPh_3)_2(C_2H_4)$ in conjunction with CF_3CO_2H or H_2SO_4[426] catalyzes the dimerization of propylene. $Ni(i\text{-}PPr_3)(C_2H_4)_2$ and $Ni(i\text{-}PPr_3)_2(C_2H_4)$ with $BF_3{\cdot}OEt_2$[122] also convert propylene into dimers. Treating the same complexes with $AlBr_3$ or HCl gives complexes which dimerize propylene. However, the bis(ethylene) complex with $TiCl_4$ or WCl_6 gives rise to trans C_6 products from propylene.[123] $Ni(i\text{-}PPr_3)(C_3H_6)_2$ reacts with BF_3 at low temperatures like −78 °C. During this reaction coordinated propylene is dimerized selectively to 2,3-dimethyl-1-butene[429] (eq 20).



(20)

This observation leads to the conclusion that propylene ligands in the starting complex are coordinated rigidly in a "methyl to methyl" orientation and are not capable of free rotation relative to the coordination axis at −78 °C. The final adducts are active catalysts of olefin dimerizations.

Addition of $AlCl_3$ in chlorobenzene solution to $Ni(CO)_2(PPh_3)_2$ results in removal of two triphenylphosphine ligands and produces an active nickel catalyst for propylene dimerization.[430] With $BF_3{\cdot}OEt_2$ also the same carbonyl complex can convert propylene into dimers.[423] The activity of various cocatalysts decreases in the order $NbF_5 > SbF_5 > TaF_5 > BF_3{\cdot}OEt_2 > AlCl_3 > InBr_3$. The surprising fact is that even in the presence of a hundredfold excess of Lewis acid no free acid remains in the medium possibly because the Friedel–Crafts behavior of these compounds may be suppressed by trace amounts of nickel.

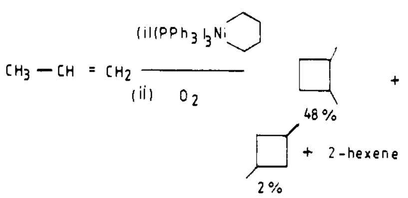
$Ni[P(OPh)_3]_4$ with $AlCl_3$ or $AlBr_3$,[431] $Ni[P(OEt)_3]_4$,[426,432,433] and $Ni(CO)_2[P(OPh)_3]_2$[430] are also active for the conversion of propylene to C_6 and substituted C_5 olefins. $Ni(C_2H_4)[P(OC_6H_4R)_3]_2$ (R = o-Me, o-OMe) are the most active.[426]

Studies of the dimerization of propylene in the presence of catalytic systems based on phosphine complexes of nickel(I) are reported.[420,421] Formation of active complexes containing alkylaluminum compounds like $AlEt_3$, Et_2AlCl, and $Et_3Al_2Cl_3$ with $NiCl(PPh_3)_2$ have been observed for propylene dimerization.[424] $Ni(PPh_3)_2Cl$ or $NiCl(PPh_3)_3$ and the $BF_3{\cdot}OEt_2$ system is also efficient for the conversion of propylene to dimers. Addition of Brønsted acids increase the catalytic activity.

Nickel(II) phosphine complexes like $NiCl_2(PPh_3)_2$ and $NiCl_2(PBu_3)_2$ with $R_{6-x}Al_2Cl_x$ (x = 2, 3, or 4) form active complexes for the dimerization of propylene. The degree of isomerization of propylene dimers[434] to 2,3-dimethyl-1-butene and -2-butene during propylene dimerization in the presence of $NiCl_2(PCy_3)_2$–$(i\text{-}Bu)_2AlCl$ increases in the order of solvents $C_6H_5CH_3 < m\text{-}Br_2C_6H_4 < C_6H_5Br < o\text{-}Cl_2C_6H_4$. Halogenated hydrocarbons participate in the regeneration of the catalytic complexes and also allow secondary cationic oligomerization of propylene.

The 1:2 HNiCl and $P(i\text{-}Pr)_3$ complex with $Et_3Al_2Cl_3$[124] is reported to catalyze the dimerization of propylene. $Et_3Al_2Cl_3$ apart from participating in the formation of active catalytic species maintain an adequate concentration of HNiCl. Apart from the catalytic conversion of propylene into linear dimers tris(triphenylphosphine)tetramethylenenickel(II) can produce cyclo dimers by oxidation of the complex prepared from the olefin.[145,150]

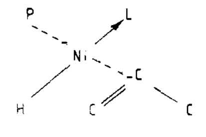
The dimerization of propylene by means of the $NiCl_2L$–$EtAlCl_2$–$0.5PBu_3$ (L = tetramethylcyclobutadiene) complex[150,301,435] is faster in chlorobenzene than in benzene. The rate of the reaction also depends upon the nature of Lewis acid. Moreover the ratio of the rate of isomerization to dimerization increases with the dielectric constant of solvents. So when unisomerized dimers are wanted, the dimerization is better conducted without a solvent (eq 21).



(21)

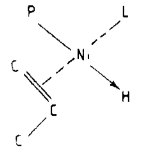
A selective dimerization of propylene to 2,3-dimethylbutene[436] catalyzed by $R_4P[(i\text{-}Pr_3P)NiCl_3]$ with $Et_3Al_2Cl_3$ in a toluene medium is reported. 2- and 4-methyl-1-pentene are the other products. The increasing temperature (−20 to +20 °C) leads to the formation of C_9 olefins at the expense of 4-methyl-1-pentene. This suggests a secondary codimerization of the product olefin with propylene. Most of the olefins are the thermodynamically less favored α-olefins indicating the absence of double-bond isomerization under these conditions. The Al/Ni ratio, although having a pronounced effect on reaction rate and yield at low values, has no influence on the catalyst selectivity.

Different cocatalysts such as $R_2Al_2Cl_4$ or $R_4Al_2Cl_2$ produce a comparable catalyst with a somewhat decreased activity. The high rates of reaction in nonpolar solvents make the presence of ionic intermediates unlikely. Use of other solvents such as benzene or chlorobenzene do not produce any major change in the product composition. The active species **34** and **35** are formed by the reaction of the monomer with a coordinated nickel hydride.



34

P = Triisopropylphosphine



35

L = Lewis acid complexed halide ligand

The nickel–butadiene complex deposited on PCl_3-treated Al_2O_3 and activated with $AlEt_3$[437] shows good catalytic activity for the dimerization of propylene giving predominantly 2-methyl-2-pentene in halogenated hydrocarbons and 4-methyl-2-pentene in pentane. The Ni/Al ratio of 1:200 is optimum for the above conversions.

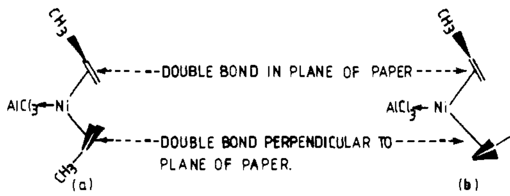
Diethyl(bipyridyl)nickel(II) activated as a catalyst[438] for the propylene dimerization by the addition of a Lewis acid such as $EtAlCl_2$ or Et_2AlCl with an Al/Ni ratio of 2–4 shows high catalytic activity in chlorinated aromatic solvents only. However, aryl(bipyridyl)nickel halide complexes activated by the addition of $EtAlCl_2$ do not require such chlorinated aromatic solvents in order to exhibit high catalytic activity. o-Chlorodiphenyl(bipyridyl)nickel chloride shows highest catalytic activity among the various aryl(bipyridyl)nickel halide complexes tried. The coordination of 2,2′-bipyridyl in the active species is not clear.

The requirements for selectivity toward a particular product isomer in the dimerization of propylene[439] have been investigated by using a square-planar nickel(II) complex with a chelating Schiff base and similar ligands and an alkylaluminum in the presence of a phosphorus atom containing additives. Steric and electronic effects are separated. The observed electronic preference for the anti-Markovnikoff mode of reaction is discussed on the basis of the Chatt model of olefin coordination taking into account the unsymmetrical nature of the propylene π and π^* molecular orbitals.

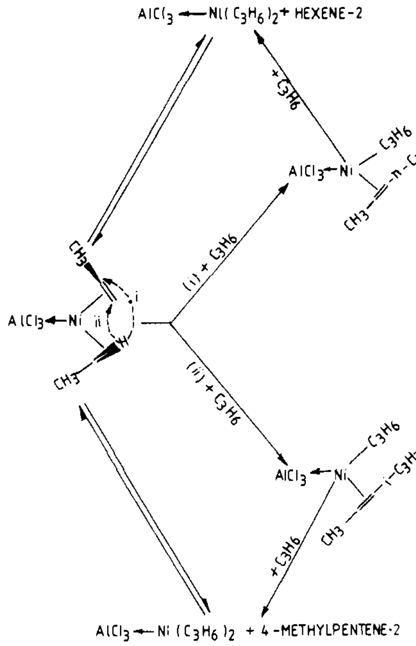
By mixing $Ni(CO)_4$, various phosphines, and $AlCl_3$ in a suitable solvent, catalysts that are active toward the dimerization of propylene[440] are formed. The maximum activity is obtained with a phosphine/aluminum ratio of 2. In a trigonally hybridized nickel (propylene)$_2$–$AlCl_3$ complex formed, the coordinated $AlCl_3$ serves to lower the electron density of the nickel, thereby facilitating the π-bonding of two propylene molecules to the central nickel atom. The complexed olefin moieties are allowed to rotate freely around the metal–olefin bond enabling them to attain sterically suitable orientation which will allow the dimerization to proceed.

The two orientations favored are "transoid" and "cisoid" geometries (Scheme XXVI). The dimerization of the two coordinated propylene units can take place through a concerted electronic rearrangement with a concomitant hydride shift. The electronic rearrangement can take place via metal d orbitals of suitable symmetry. The mechanism for the two orientations are shown in Schemes XXVII and XXVIII.

SCHEME XXVI. The "Transoid" (a) and "Cisoid" b) Orientations of the Nickel-Bis(propylene) -Aluminum Chloride Complex



SCHEME XXVII. Dimerization Mechanism for the "Transoid" Orientation



The $NiCl_2$–$AlCl_3$ (1:1) complex in the presence of $AlPr_3$ is an effective homogeneous dimerization catalyst for propylene.[384] Treating $NiCl_2$ on a solid carrier with $AlPr_3$, $Et_3Al_2Cl_3$, or $(i\text{-}Bu)_2AlCl$ gives a heterogeneous dimerization catalyst of activity comparable to that of the homogeneous catalyst. Catalysts prepared from nickel poly(4-vinylpyridine) complexes[137] in an ethylene–propylene–norbornene polymer and alkylchloroaluminums also have been used for the dimerization of propylene. These catalysts are stable over a wide temperature range. Their activity increases with the increasing ability of the solvent to swell the polymer.

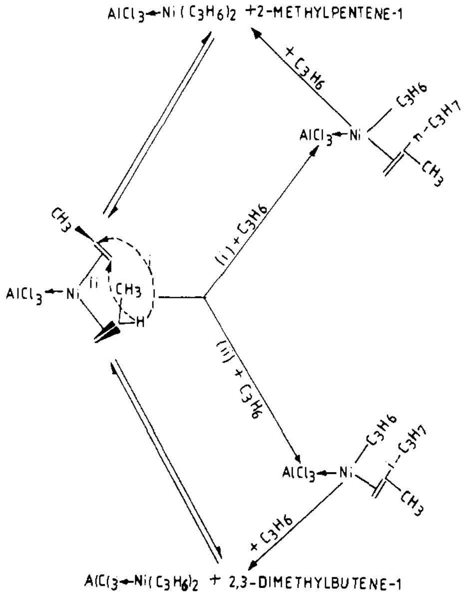
4. Rhodium

$RhCl_3 \cdot 3H_2O$ is reported as a propylene dimerization catalyst in the presence of additives like alcohol[161] and nitrobenzene.[337] $Rh_2Cl_2(SnCl_3)_4$ is effective at 50–70 °C and 1.5–40 atm of propylene.[339] However, addition of 2–3 mol/L of HCl decreases the pressure required and increases the rate and selectivity of the reaction.

5. Palladium

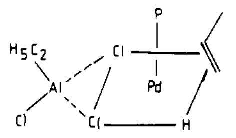
$PdCl_2$ is used as a catalyst for the dimerization of propylene[171,173] in the presence of various solvents like chloroform, dichloromethane, and anisole. In all cases

SCHEME XXVIII. Dimerization Mechanism for the "Cisoid" Orientation



high proportions (65–90%) of straight chain hexenes are formed. However, in the presence of a cocatalyst like $EtAlCl_2$ and additives (PPh_3, $AsPh_3$, or $SbPh_3$) 2-methylpentene is the predominant product.[438] Pd(olefin)Cl_2[171] catalyzes the reaction to give 100% *n*-hexene selectively. When Pd(BZCN)Cl_2 is used, straight chain products are formed. This is associated with the isomerization of olefin. A mechanism involving a hydridopalladium(II) compound as the catalytically active species is suggested.

A homogeneous catalyst solution made up of Pd(acac)$_2$, PR_3, and $EtAlCl_2$ in 1,2-dichloroethane[441] dimerizes propylene selectively up to 95% linear hexenes although at relatively low reaction rate. Replacement of the phosphine by a phosphite increases the rate but considerably lowers the selectivity. The ratio of P/Pd is critical (P/Pd = 2). At $P/Pd \geq 5$ no catalytic activity is observed, presumably due to the blocking of free sites. Relatively high ratios of Al/Pd are required, indicating that the catalytic species is formed in an equilibrium reaction. Activity is found for $5 \leq Al/Pd \leq 25$ with an optimum around 20. **36** is the proposed structure for the active species where P is the phosphine.



36

I. Rare-Earth Elements

1. Cerium

There are two patents[442,443] on the use of an acetylacetonate complex of the first member of lanthanides for propylene dimerization. According to them a mixture of Ce(acac)$_3$, PPh_3, and chlorobenzene is stirred at 24–29.5 °C. To this is added $Et_3Al_2Cl_3$, and propylene is fed at higher (600 psi) and lower (<150 psi) pressures and the mixture stirred to give the dimers. The yield of dimers is less in the absence of PPh_3.

2. Thorium

Thorium nitrate on treatment with PPh_3 in chlorobenzene solvent[444,445] and subsequent mixing with $Et_3Al_2Cl_3$ generates the active catalyst which can dimerize propylene at 150–500 psi and at 115–120 °F to give the dimerized products.

Table IV deals with the published and patent data on the dimerization of propylene. Available kinetic data are summarized in Table V.

V. Criteria for Catalytic Activity[6]

(A) Titanium metal based complexes are versatile catalysts for the dimerization of olefins. Other commonly used catalysts have been based on the group VIII elements. Of them Fe, Co, Ni, Ru, Rh, and Pd are particularly active.

(B) For olefin activation it is necessary for the metal to be sufficiently "soft" in nature. So elements of the first transition series (Fe, Co, and Ni) are generally active when bonded with less than two "hard" anions. From higher oxidation states the necessary "reduction" can be effected by a variety of alkyl derivatives of aluminum and magnesium or by other reducing agents. Presence of a Lewis acid enhances the reducing power of some derivatives. For elements of the second transition series the situation is complex because of their "soft" character even in higher oxidation states. Reduction can also be achieved by means of other organic compounds like hydroxylic solvents or the monomer itself.

(C) The addition of "soft" ligands like phosphine may provide better selectivity. Phosphines can also influence the mode of linkage of monomer to the metal.

(D) Addition of Lewis acids to a given catalytic system results in either an increase of the reaction rate or a profound modification of the course of the reaction. The effect is specific for each metal and each type of monomer. The explanations for the "Lewis acid effects" are (1) the release of a free coordination site in the transition metal, for example, by the dissociation of a dimeric complex or the competition for anionic and neutral ligands; (2) an increase in the positive charge carried by the metal, and (3) the release of a proton.

(E) Solvents either promote the catalytic activity owing to their reducing power or enhance the dimerization rate. The nature of the solvent is somewhat critical. If it is too "soft", it competes with the olefin for coordination, and if it is too "hard", it can neutralize the needed Lewis acidity. In several cases the dimerization rate increases with the dielectric constant of the medium consistent with the nature of the ionic complex.

VI. Conclusions

A majority of the title reactions operate in the liquid phase in the presence of a Ziegler-type catalytic system

TABLE IV. Selected Studies on Dimerization of Propylene by Transition-Metal Complexes

cat. system	reactn conditns	products	comments	ref
		Boron		
$(C_4H_9)_3B$-MR_n-mH_m (M = Al, Ga, In, Be; R = alkyl; *n* = valence of metal; *m* = 0–3)	195–200 °C	2-methyl-1-pentene		359
		Aluminum		
$[(CH_3)_2CH]_3Al$	170–200 °C, 150–200 atm	2-methyl-1-pentene		360–364
organoaluminum compounds			E_a = 11.7 kcal/mol	370
organoaluminum compounds			E_a = 14 kcal/mol	371
$(C_2H_5)_3Al$	dehydronaphthene, 250 atm, 300 °C	2-methyl-1-pentene, (90%)	Al/C_3H_6 = 0.023	446, 447
$(C_2H_5)AlCl_2$		propane (50%), hexene (36%), nonene (3.5%), dodecene (0.5%)		448
$(C_2H_5)_3Al$	180 °C, 170 atm	2-methyl-1-pentene (70%)		449, 450
$(C_2H_5)_3Al/H_3Al/(CH_3)_2AlH/(C_2H_5)_2AlH/(CH_3)_3Al/Ph_3Al$	200 atm, 200 °C/240 °C/300 °C/350 °C			451
$(C_2H_5)_3Al_2Cl_3$–P(O-dodecyl)$_3$	toluene, 0 °C, 45 min	hexenes, 4-methylpentenes		452
R'_nAlX_{3-n}–BiR_3 (R = R′ = alkyl; X = halogen; *n* = 1, 1.5, or 2)	toluene, 20 °C, 2 h	hexenes, 4-methylpentenes		453
$Al(OR)_3$ (R = Pr or hexyl)	180–240 °C, 150–200 atm	hexenes (major), nonene (4–5%)	cat. consumed = 0.5–0.7 kg of Al/ton of crude hexene; product yield is 2 tons/day	454
$(C_2H_5)_3Al$ or $[(CH_3)_2CHCH_2]_3Al$	isooctane, 225–250 °C, 120–200 atm, 1.5–2.0 h	2-methyl-1-pentene (85–90%), 2-methyl-2-pentene, higher olefins (traces)		455
		Titanium		
$(TiOR)_4$–$(C_2H_5)_3Al$		unspecified dimers	$AlR_3/Ti(OR)_4 < 10$	46
$Ti(OR)_4$–$(C_2H_5)_3Al$	chloroalkanes, 0–50 °C, 1–10 atm	4-methyl-1-pentene, 4-methyl-2-pentene		210, 211, 456
$Ti(OR)_3(acac)$–AlR_3 (R = Bu, *i*-Pr)	heptane, 60 °C, 9 kg/cm^2, 5 h	4-methyl-1-pentene (43%), 4-methyl-2-pentene (1.8%), *n*-hexene (9%), 2-hexenes (46.4%)		374
CH_3TiCl_3–$(CH_3)AlCl_2$	CH_2Cl_2/toluene, −70 °C			78, 375
$(\eta$-$C_4H_6)_2Ti(dmpe)$		2,3-dimethyl-1-butene		81
		Chromium		
$CrCl_3(py)_3/CrCl_3(4Etpy)_3/CrCl_3(PBu_3)_2$–$(C_2H_5)AlCl_2$	50 °C, 100 psig, 1.5 h	2-methylpentenes (69%), *n*-hexenes (31%), nonenes and dodecenes are minor		99, 101
		Manganese		
$MnCl_2$–$[(CH_3)_2CH]_3Al$–$AlCl_3$		2-methyl-2-pentenes, 4-methyl-2-pentenes, 2-hexenes		384
		Iron		
R_pFe–R'_mAlX_{3-m}–phosphine (R = acyl, allyl, cyclopentadienyl; p = metal valence; R = alkyl or aralkyl; x = halogen; m = 1–3)	*n*-heptane/benzene, −10 to 50 °C, 11 atm			105
$Fe(acac)_n$–$(C_2H_5)_2AlCl$–COD (*n* = 2 or 3)	heptane/toluene	2-methyl-2-pentene		386
$Fe(acac)_2$–$(Me_2CHCH_2)_2AlCl/(C_2H_5)_2AlCl/(C_2H_5)AlBr_2$		4-methyl-1-pentene, 4-methyl-2-pentenes, 2-methyl-2-pentenes, *n*-hexenes (major) and 2-methyl-1-pentene, 2,3-dimethylbutenes (minor)		385

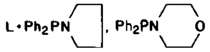
$FeCl_3$–Pr_3Al–$AlCl_3$		2-methyl-2-pentenes, 4-methyl-2-pentenes, 2-hexenes		384
		Cobalt		
$CoCl_2$–$(C_2H_5)_2AlCl/R_3Al/AlCl_3$–$AlCl_3$	CH_2Cl_2, 40–80 °C, 150 °C	hexenes (30%), methylpentenes (70%)	selectivity to dimers is 95%	384, 387
$CoCl_2$–$(C_2H_5)_{6-x}Al_2Cl_x$ (x = 2, 3, or 4)	heptane, 40 °C, 43 atm, 16 h	hexenes, 2,3-dimethylbutenes, 2-methylpentenes		107, 457–463
$CoCl_2$–Charcoal–$(C_2H_5)_2AlCl$		hexenes		464
R_pCo–R'_mAlX_{3-m}–phosphine (R = acyl, allyl, or cyclopentadienyl; p = metal valency; R = alkyl or aralkyl; x = halogen; m = 1–3)	n-heptane/benzene, −10 to 50 °C, 1–10 atm			105
$CoHN_2(PPh_3)_3/CO(N_2)(PPh_3)_3$	benzene, 20 °C, 1 atm	2-methyl-1-pentene (65.3%), *trans*-4-methyl-2-pentene (17%), 2-methyl-2-pentene (2.7%), *trans*-3-methyl-2-pentene (0.2%)		109, 388, 394, 465
		cis-3-mthyl-2-pentene (0.1%), 2,3-dimethyl-1-butene (2.4%), 2,3-dimethyl-2-butene (1.4%), 3-methyl-1-pentene and 4-methyl-1-pentene (2.8%), *cis*-4-methyl-2-pentene (1.2%), 3-methyl-1-butene (4.0%), 2-methyl-1-butene (2.7%), 2-methyl-2-butene (0.6%)	E_a = 22.9 kcal/mol; ΔH = 22.3 kcal/mol; ΔS = 13 cal/(mol·K)	
$(Co(PBu)_3)_2Cl_2$–$R_{6-x}Al_2Cl_x$		dimethylbutenes		466
L_2CoX_2–$(C_2H_5)AlCl_2$ (L = quinoline, isoquinoline, PPh_3, pyridine; X = Cl, Br)	chlorobenzene, 23.2–24.2 °C, 30 psig, 6 h	2-methylpentenes (70.8%), hexenes (25.3%), 2,3-dimethylbutenes (5.7%)		467
L_2CoX_2–$(C_2H_5)AlCl_2$ (L = pyridine, 4-Et-pyridine, quinoline, PPh_3; X = Cl, Br)	chlorobenzene, 30 psig, 10–25 °C, 18.5 h	2-methylpentenes (67.3%), hexenes (30.7%)		468
$Co(acac)_2$–$(C_2H_5)_2AlCl/(C_2H_5)AlCl_2$–COD	heptane/toluene/$CHCl_3$	2-methyl-2-pentenes		366
$Co(acac)_2$–$HAl(C_2H_5)_2$–L–COD 	methylpentenes, 25 °C, 3 bar, 6 h	2-methyl-1-pentene (85%)		469
$Co(acac)_2$–$(C_2H_5)AlBr_2/(i\text{-}C_4H_9)_2AlCl/(C_2H_5)_2AlCl/(C_2H_5)_3Al_2Cl_3/(C_2H_5)AlCl_2$		4-methyl-1-pentene, 4-methyl-2-pentenes, 2-methyl-2-pentenes, n-hexenes, 2-methyl-1-pentene, 2,3-dimethylbutenes		385
		Nickel		
nickel salt–$R_{6-x}Al_2Cl_x$–PR_3 (x = 2, 3, or 4)	−20 to 50 °C, 1–5 atm	2-methyl-1-pentene, hexene, *cis*-2-hexene, *trans*-2-hexene, 4-methyl-2-pentene		388, 470–472
$[(\pi\text{-allyl})NiX]_2$		n-hexenes (20–30), 2-methylpentene (68–78%), 2,3-dimethylbutene (2–6%)		143, 240, 243
$[(\pi\text{-allyl})NiX]_2$–$AlX_3$–$PR_3$		n-hexene, 2-methylpentene, 2,3-dimethylbutenes		5, 30, 107, 147, 149, 398, 399
$[(\pi\text{-allyl})NiX]_2$–$TiCl_4/MoCl_5/VoCl_4/WCl_6$		n-hexenes, 2-methylpentenes, 2,3-dimethylbutenes		30, 107, 147, 149, 241, 459
$(\pi\text{-allyl})NiBr$–PCy_3–$(C_2H_5)AlCl_2$	−75 °C/−55 °C	higher olefins (10–15%), 4-methyl-1-pentene (18%), *cis*-4-methyl-2-pentene (1.3%), 2,3-dimethyl-1-butene (76%), 2-methyl-1-pentene 4%)		402
$(\pi\text{-crotyl})NiCl_2$–$TiCl_4$–$PPh_3$		2-methyl-2-pentene	E_a = 15.2 kcal/mol	403

TABLE IV (Continued)

cat. system	reactn conditns	products	comments	ref
(π-allyl)NiBr–$AlBr_3$–PPh_3/PCy_3	chlorobenzene, –40 to 0 °C	*n*-hexenes (20%), 2-methylpentenes (75%)	reaction rate = 4600 g of propene/g of Ni/h; yield is 95.3%	473
cross-linked resins containing difluoroacetic group supported η^3-allylic nickel complexes–$(C_2H_5)AlCl_2$	chlorobenzene, 25 °C	2,3-dimethylbutenes (2%), methylpentenes (67%), hexenes (31%)	Al/Ni molar ratio = 15.5; conversn of propylene is 95%	404, 405
Al_2O_3–SiO_2 supported Ni(π-allyl)$_2$/ Al_2O_3–SiO_2–WO_3 supported Ni(π-allyl)$_2$–CH_3AlCl_2		hexenes, methylpentenes		406
NiL_2–$(i\text{-}C_4H_9)_2AlCl$–PR_3/$P(OR)_3$ (L = AcAcH$^-$, Cl$^-$, I$^-$, NO_3^-; R = alkyl, isoalkyl, Ph)	toluene/octane, 1 atm	hexenes		401, 413
Ni[Hf(acac)]$_2$–$(i\text{-}C_4H_9)_3Al$	toluene, 80 °C	hexenes (77.8%), 4-methylpentenes (4.3%), 2-methylpentenes (17.2%), 2,3-dimethylbutenes (0.8%)		474
Ni(acac)$_2$–$(C_2H_5)_3Al$/$(C_2H_5)_2(OC_2H_5)Al$/ $(C_2H_5)(OC_2H_5)_2Al$	ethers, 20–40 °C	1-hexene (4.2%), *cis*-2-hexene (32.7%), *trans*-2-hexene (28.9%), *cis*-3-hexene (6.0%), *trans*-3-hexene (5.8%), 4-methyl-1-pentene (1.7%), *cis*-4-methyl-2-pentene (2.0%), *trans*-4-methyl-2-pentene (1.8%), 2-methyl-2-pentene (10.7%), 2-methyl-1-pentene (5.6%)	selectivity to linear olefins is 78%	385, 407, 475, 476
Ni(acac)$_2$–$(C_2H_5)_3Al_2Cl_3$–PPh_3	–50 to 40 °C	2-methylpentenes, 2,3-dimethylbutenes	Ni/Al/P mole ratio = 1:45:16	411
Ni(acac)$_2$–$(i\text{-}C_4H_9)_2AlCl$–PPh_3/Pcy$_3$/ $(Me_3C)_2PBr$		4-methyl-1-pentene (23%), other dimers		412
Ni(acac)$_2$–$(C_2H_5)_3Al_2Cl_3$–R_3P (R = PhX; X = *p*-Cl, *p*-H, *p*-Me, *p*-OMe, *o*-Me)	toluene	2,3-dimethylbutenes	activity with tertiary phosphines is of the order *p*-Cl > *p*-H > *o*-Me ≈ *p*-Me > *p*-Ac > $P(C_2H_5)_3$ > PBu_3	142, 401
Ni(acac)$_2$–$(C_2H_5)_3Al_2Cl_3$–PPh_3	toluene, 30 °C	*n*-hexenes, and methylpentenes	cat./cocat./PPh_3 = 1:8:3; order with respect to propylene = 2; order with respect to cat. = 2	393, 414
Ni(acac)$_2$–$(C_2H_5)_3AlCl_3$–PPh_3	toluene, –50 to –22 °C	*n*-hexenes, methylpentenes, 2,3-dimethylbutenes	propylene/nickel mol ratio = 240–2400; rate = k [Ni][C_oH_6], E_a = 13 kcal/mol	415
Ni(acac)$_2$–$(C_2H_5)_3Al$–PPh_3–$BF_3{\cdot}OEt_2$	toluene/benzene/ chlorobenzene	methylpentenes, hexenes, 2,3-dimethylbutenes	Ni(acac)$_2$/Al$(C_2H_5)_3$/(PPh_3)/ $BF_3{\cdot}OEt_2$ = 2:1:4:35	416
Ni(acac)$_2$(COD)/Ni(acac)$_2$(C_4H_8)–polystyrene-containing PEt_2/ $P(i\text{-}Bu)_2$/$P(OEt)_2$/$P(NEt_2)_2$	alkane solvent	4-methyl-2-pentene (major)	1300–1700 g/h of dimers/g of Ni; cat. is stable >1000 h	417
Ni(acac)$_2$–$(C_4H_9)_3Al$	250 °C, 1800 psi	2-methylpentenes		477
Ni(acac)$_2$–$(C_2H_5)_2ClAl$–H_2O	5 kg/cm^2, 0° –50 °C, 5 min	dimer, higher oligomers	dimer/oligomer = 93%	478, 479
Ni(acac)$_2$–$(C_2H_5)_3Al$–PhC≡CH	xylene	2-methyl-1-pentene (53%), 2-methyl-2-pentene (41%)		480
Ni(acac)$_2$–$R_{6-x}Al_2Cl_x$ (x = 2–4)–PPh_3	CH_2Cl_2, 600 psig, 40 °C, 17 h	*n*-hexenes (31%), 2-methylpentenes, 2,3-dimethylbutenes	linear hexenes is 31%	252, 481–484
Ni(acac)$_2$–$(C_2H_5)_3Al_2Cl_3$–PPh_3	30 °C, 1.5–3.2 atm, nitrogen	C_6 alkenes (major), C_9 olefins (minor)		485
Ni(acac)$_2$–R_3Al–$BuPCl_4$	3 h	methylpentenes, 2,3-dimethylbutenes, hexenes, higher oligomers	propylene conversn to dimers is 92%	486

$Ni(acac)_2$–$(C_2H_5)_3Al$	cyclohexane, 40 °C, 53.5 atm, 16.5 h	2-hexenes (56%), 3-hexenes (13.0%), 4-methyl-1-pentene (2.0%), 4-methyl-2-pentene (4.0%), 2-methyl-2-pentene (12.0%), 2-methyl-1-pentene (6.5%)		487
$Ni(acac)_2$–$(C_2H_5)AlCl_2$–PCy_3	chlorobenzene, 9 atm, 27 °C, 2–3 min	C_6 olefins, C_9 olefins		488, 489
$Ni(acac)_2$–$(C_2H_5)_2AlCl/(C_2H_5)AlCl_2$–1,5-COD	toluene/$CHCl_3$, 85–90 °C, 40 psi	3-hexenes, 1-hexene, 2-methyl-2-pentene, 4-methyl-2-pentene, 2,3-dimethyl-2-butene, 2-hexene, 2,3-dimethyl-1-butene, 4-methyl-1-pentene	cat. efficiency is >5000 g of product/g of Ni; selectivity to hexenes is >90% in chlorobenzene solvent	386
$Ni(acac)_2$–$R_{6-x}Al_2X_x$–$BrP(CMe_3)_2$	aromatic hydrocarbon/haloaromatic hydrocarbons/CCl_4, −20 to +30 °C	4-methyl-1-pentene	P/Al/Ni ratio = 1–12:10–150:1	490
$Ni(acac)_2$–$(C_2H_5)_3Al_2Cl_3$–PPh_3	1.58 atm, 30 °C, 31.5 h	C_6 olefins	$Ni(acac)_2/PPh_3/(C_2H_5)_3Al_2Cl_3$ mole ratio = 1:8:32	491
$Ni(acac)_2$–$(C_2H_5)_3Al_2Cl_3$–PCy_3	chlorobenzene, −25 °F, 1 h	methylpentenes (36.9%), 2,3-dimethyl-1-pentene (60%), 2,3-dimethyl-2-butene (1.2%), *n*-hexene (1.0%)		492
$Ni(acac)_2$–$(C_2H_5)_2AlCl$–P_2O_5		methylpentenes, dimethylbutenes, hexenes	P/Ni/Al = 5:1:10	493
$Ni(acac)_2$–$(C_2H_5)_2Al(OC_2H_5)$–PPh_3		2-hexene, 1-hexene, 2,3-dimethylbutenes		496
$Ni(acac)_2{\cdot}xH_2O$–$(C_2H_5)_2Al(OC_2H_5)$	toluene, 40 °C, 680 psig, 17.25 h	hexenes (80%)	linearity 76%	494, 495
$Ni(acac)_2$–$(C_2H_5)_2Al(OC_2H_5)$–$(C_2H_5)_4Sn/(C_4H_9)_4Sn$	heptane, 40 °C, 600 psig	unspecified dimers		476
$Ni(L_2)$–$(C_2H_5)_2Al(OC_2H_5)$ (L = $CF_3COCH_2COCF_3$)	toluene, 58–60 °C, 1.6 h	*n*-hexene (72–80%), nonenes (20%), dodecenes (0.2%)	propylene conversn is 80%	267
$Ni(acac)_2$–$(C_2H_5)_2AlCl/(C_2H_5)AlCl_2$–$PBu_3$	hexane/chlorobenzene, 59–63 °F	methylpentenes (69%), *n*-hexenes (11%), 2,3-dimethylbutenes (20%)	cat. efficiency is 38 000 g/g of Ni, selectivity to C_6 olefin is 85%	497
$Ni(PhCOCHCOPh)_2$–$(C_2H_5)_2Al(OC_2H_5)$	ethylene glycol–dimethyl ether–toluene, 40 °C, 17 h	linear hexenes (77%)		498
polymer gel immobilized $Ni(acac)_2$–$(C_2H_5)AlCl_2/(C_2H_5)_2AlCl$	*n*-heptane/2,2,4-trimethylpentane	hexenes		276, 409
$Ni(acac)_2$ and an inorganic Ni salt supported on Al_2O_3/SiO_2–$[(CH_3)_2CHCH_2]_2AlCl$		C_6 olefins	activity decreases in the order $NiCl_2 > NiBr_2 > Ni(NO_3)_2 > NiSO_4$	410, 499
$Ni(acac)_2$ on alkaline earth metal carbonate or oxide–$R_{6-x}Al_2Cl_x$	organic solvents	hexenes		500
$Ni(acac)_2$ supported on Al_2O_3 or aluminosilicate–$(C_4H_5)_3Al_2Cl_3$–$(i\text{-}Pr_3)P$		C_6 olefins (67–85.0%), C_9 olefins (13.0–27.8%), higher oligomers (2–6.4%)	major products are C_6 olefins (2,4-dimethyl-1-butene)	501
$Ni(acac)_2$ supported on SiO_2–Al_2O_3–$R_{6-x}Al_2X_x$–PR_3	144 °F, 120 psig, 3 h	2-methylpentene (35.4%), hexenes (12.6%), 2,3-dimethylbutenes (0.6%), higher oligomers (44.5%)		502, 503
$Ni(O_2CR)_2$–$(C_2H_5)_2AlCl$ (RCO_2H = octenoic acid, oleic acid)		hexenes, nonenes, and dodecenes (minor)		419, 504
Ni oleate–i-Bu_2AlCl	*tert*-butyltoluene, <20 °C, 1.5 Kg/cm^2	2-methyl-2-pentene (72.7%), *cis*- and *trans*-4-methyl-2-pentene (11.9%), 1-hexene (7.8%), *cis*-dimethyl-2-butene (7.4%), 4-methyl-1-pentene (0.2%)	conversn to dimers is 90%	505
$Ni(O_2CR)_2$–$(C_2H_5)AlCl_2$–CF_3CO_2H (RCO_2H = C_9–C_{13} carboxylic acids)	isooctane, 15 bar, 42 °C, 3 days	hexenes, nonenes	91% conversn of propylene in the presence of CF_3CO_2H and 70% conversn in the absence of the additive	506

TABLE IV (Continued)

cat. system	reactn conditns	products	comments	ref
$Ni(OAc)_2$–$(C_2H_5)AlCl_2$–PhSSPh	chlorobenzene, 20 °C	4-methyl-1-pentene (0.4%), *cis*-4-methyl-2-pentene (1.2%), *trans*-4-methyl-2-pentene (9.6%), 2-methyl-1-pentene (6.3%), C_9 olefins		270
$Ni(O_2CR)_2$–$R_{6-x}Al_2X_x$–PPh_3/PX'_3 (X′ = halogen, alkoxy group)	0 to 10 °C, 1 atm	C_6 olefins	≤90% selectivity to methylpentenes	324, 325, 418
$Ni(O_2CR)_2$–$(C_2H_5)_2AlF$ (HO_2CR = oleic acid, isopropylsalicylic acid)	heptane, 50 °C, 72 min	*n*-hexene (40–51%), 2-methylpentenes (45–57%), 2,3-dimethylbutenes (2–4%)	37.6% conversn	107, 145, 146, 459, 507
$Ni(O_2CH)_2$–$(C_2H_5)_2AlCl_2$	40 °C, 3 h	2-methyl-2-pentenes		478
$Ni(O_2CR)_2$–$(C_2H_5)_3Al_2Cl_3/(C_2H_5)AlCl_2$ (RCO_2H = isopropylsalicylic acid, C_{17} acid)	isooctane, −20 to 20 °C, 1 h	*cis*-2-hexene (2.3–5%), *trans*-2-hexene (2.3%), 1-hexene (7.3%), 2,3-dimethyl-1-butene (6.3%), 2,3-dimethyl-2-butene (0.4%), 2-methyl-1-pentene (5–22.5%), 3-methyl-1-pentene and 4-methyl-1-pentene (0.3–2%), 2-methyl-2-pentene (10–51.8%), *cis*-4-methyl-2-pentene (1.7–6.6%), *trans*-4-methyl-2-pentene (10.3–50.3%)		323
$Ni(O_2CR)_2$–$(C_2H_5)_3Al_2Cl_3$ (RCO_2H = *p*-toludine-*m*-sulfonic acid, *o*-aminobenzenesulfonic acid)	toluene, argon, 50 °C, 12 h	4-methyl-1-pentene (1.8%), 4-methyl-2-pentene (53.1%), 2-methyl-1-pentene (3.8%), 2-methyl-2-pentene (18.5%), 1-hexene (17.7%), 3-hexene (4.1%), 2,3-dimethylbutenes (1.2%)	86% selectivity to dimers; total conversn is 87% of propylene	508
$Ni(O_2CR)_2$–$(C_2H_5)_{6-x}AlX_x$–$PPh_3/PCl_3/P(i\text{-}Pr)_3$ (CO_2H = naphthenoic acid)	toluene, 20 °C, 5 bar, 1–5 h	*n*-hexene, 2-methylpentene, 2,3-dimethylbutenes, 4-methylpentenes	yield of dimers is 82.2% of propylene	509–512
$Ni(O_2CR)_2$–$AlCl_3$–$(C_2H_5)_3Al$ (RCO_2H = octenoic acid)	toluene, 10 °C	2-methyl-2-pentene (major)	yield of dimers is 96.1%	513
$Ni(O_2CR)_2$–PCl_3–$(C_2H_5)_3Al$ (RCO_2H = octenoic acid)	toluene, 1 h, 0 °C	2-methyl-1-pentene (6%), 2-methyl-2-pentene (55%), 4-methyl-1-pentene (0.4%), 4-lmethyl-2-pentene (16%), 2,3-dimethyl-1-butene (3%), 2,3-dimethyl-2-butene (14%), *trans*-2-hexenes (5.5%)	yield of dimers is 86.7%	514
Ni octenoate–$(C_2H_5)_3Al$–$BF_3{\cdot}Et_2O$	toluene, 50 °C, 1 h	dimer (92%)		515
$Ni(CH_3COCH_2CO_2)_2$–$(C_2H_5)_2AlCl$–$C_2H_5AlCl_2$	2-methyl-1-pentene/4-methyl-2-pentene, 25 °C, 1 h	2-methyl-2-pentene		227
$Ni(O_2CR)_2$–$(C_2H_5)_3Al$–$SnCl_4$ (RCO_2H = octenoic acid)	toluene, 10 °C		yield of dimers is 87.7%	516
$Ni(O_2CR)_2$–$(C_2H_5)_3Al/[(C_2H_5)_2Al]_2O$–$PCy_3$/isoprene ($RCO_2H$ = naphthenoic acid)	toluene, 20 °C, 4 kg/cm^2, 3 h	mixture of dimers	conversn to dimers is 79.4%, selectivity to α-olefins is 58.7%	238, 517, 518
$Ni(Bu)(CS_2O)$–$(C_2H_5)_2AlCl$–H_2O	5 kg/cm^2, 0–50 °C, 5 min	2-methyl-2-pentene, 4-methylpentenes, other dimers and oligomers	dimer/oligomer = 93%	478, 479
$NiCl_2(PPh_3)_2$–$R_{6-x}Al_2X_x$ (x = 2, 3, or 4)	toluene, 20 °C	*n*-hexene, 2-methylpentenes, 2,3-dimethylbutenes, 4-methyl-2-pentenes (85%), C_9 olefins (15%)		280, 619
$NiCl_2{\cdot}2[PPh(cyclohexyl)_2]$–$(C_2H_5)_2AlCl$–$H_2O$	0 °C, 1 h	4-methyl-1-pentene (10%), *cis*-4-methyl-2-pentene (13.2%), *trans*-4-methyl-2-pentene (15.25%), 2,3-dimethyl-1-butene (43.1%), 2-methyl-1-pentene (13.3%), *n*-hexene (3.3%)	conversn is 80%	520
$NiX_2(PR_3)_2$–$R_{6-x}Al_2X_x$ (X = Cl, Br; R = Bu, Ph; x = 2, 3, or 4)	chlorobenzene	C_6 olefins	cocat./cat. = 2	253, 281, 510, 521
$NiCl_2(PPh_3)_2/NiCl_2(PPh_2H)_2/$	0–25 °C	C_6 olefins		466, 522

$NiCl_2(dppe)/NiCl_2(PCy_3)_2/NiBr_2(PCy_3)_2/NiCl_2(P\text{-}i\text{-}Pr_3)_2$–$(C_2H_5)_3Al_2Cl_2/(C_2H_5)_2AlCl/C_2H_5)AlCl_2$				
$NiCl_2(PBu_3)_2$–$(C_2H_5)_2AlCl/(C_2H_5)AlCl_2$–$(CH_3)_3CCl$	61.8 °C, 25 kg/cm^2	2,3-dimethylbutenes, 2-methylpentenes, *n*-hexenes	Al/Ni ratio = 19.9:1; conversn of propylene is 93.4%; selectivity to dimers is 82.4%	283, 509, 523, 524
$NiCl_2(PPh_3)_2$–$(C_2H_5)AlCl_2$–$(PPh_3)_2Mo(NO)_2Cl_2$	50 psi, 25 °C	C_6 olefins (30.3%) and higher olefins		525
$NiCl_2(Ph_2PCH{=}CHPPh_2)$–$(C_2H_5)AlCl_2$	chlorobenzene, 16–20 °C, 30 psig, 1.5 h	C_6 olefins		526
$NiSO_4(PPh_3)_2$–$CH_3AlCl_2/(C_2H_5)AlCl_2$	−10 to 10 °C	2-methyl-2-pentenes	Al/Ni ratio = 5:20	527
$NiCl_2(i\text{-}PPr_3)_2$–$(C_2H_5)_3Al_2Cl_3$–$C_7H_{16}N$	chlorobenzene, 0 °C, 860 mm	2,3-dimethylbutenes	Al/Ni ratio of 20:1 is used; rate = 250 kg of product/h/g of Ni	501, 528
$NiCl_2(PPh_3)_2$–$(C_2H_5)AlCl_2$	chlorobenzene, 25 psig, 0–5 °C, 2 h	2,3-dimethylbutene (13.2%), 2-methylpentenes (72.0%), *n*-hexenes (14.8%)	conversn to dimers is 86%	529
$NiCl_2(i\text{-}PPr_3)_2$–$(C_2H_5)_3Al/(C_2H_5)_3Al_2Cl_3$	heptane/chlorobenzene, 0 °C, 100 mm	C_6 olefins (90%), C_9 olefins (10%)	Al/Ni = 2:1 for $(C_2H_5)_3Al$; Al/Ni = 4:1 for $(C_2H_5)_3Al_2Cl_3$	530
$NiX(PPh_3)_3$–$AlCl_3$		*n*-hexenes, 2-methylpentenes, 2,3-dimethylbutenes		297
$NiCl_2(PPh)_3$–$AlCl_3$–$(C_2H_5)_3N$–Ph_3P/Bu_3P	PhCl, 20 °C	4-methyl-1-pentene, 4-methyl-2-pentene, 2-methyl-2-pentene (major product), 2,3-dimethylbutene		531
$NiCl(PPh_3)_2/NiCl(PPh_3)_3$–$BF_3{\cdot}OEt_2$–Brønsted acids		hexenes, methylpentenes		422, 423, 532
$NiCl_2(PR_3)_2$–$(i\text{-}C_4H_9)_2AlCl$ (R = cyclohexyl)	halogenated hydrocarbons	2,3-dimethylbutenes	isomerization increases in the order when R = PhMe < $m\text{-}Br_2C_6H_4$ < PhBr < $o\text{-}Cl_2C_6H_4$	434
$HNiCl(i\text{-}PPr_3)_2$–$(C_2H_5)_3Al_2Cl_3$		C_6 olefins	highest activity for $Et_3Al_2Cl_3$	124
$NiCl_2(PBu_3)_2$ deposited on SiO_2–Al_2O_3–$(C_2H_5)_2AlCl$		hexenes, 2,3-dimethylbutenes, 2-methylpentenes		286
$NiClCPh_3$–$AlBr_3$–PPh_3	chlorobenzene	dimer and trimer (small amounts)		533
$Ni(PR_3)_2(ethylene)$–$AlCl_3$		*n*-hexene, 2-methylpentenes, 2,3-dimethylbutenes		297
$Ni(PEt_3)_2(CF_2{=}CF)Cl$–$(C_2H_5)AlCl_2$	9.2 °C, 30 psig, 30 min	C_6 olefins		534
$Ni(COD)_2$–$(C_2H_5)_3P$/2-Cl-1,3-butadiene/$p\text{-}ClC_6H_4COCl$		C_6 olefins		535, 536
$NiCl_2L_2$–$R_{6-x}Al_2Cl_x$–PR_3 (L = tetramethylcyclobutadiene)	chlorobenzene/benzene	*n*-hexenes, 2-methylpentenes, 2,3-dimethylbutenes		150, 300, 301, 435
$Ni(CH_2{=}CHCN)_2$–$R_{6-x}Al_2Cl_x$–PR_3	toluene, 5 °C, 45 min	4-methyl-1-pentene, 2-methyl-2-pentene, 2-methyl-1-pentene, 2-hexene, 3-hexene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene		537, 538
$Ni(ethylene)[(P(OC_6H_4R)_3]_2$ (R = Me, OMe)/$Ni(ethylene)(PPh_3)_2$–$(C_2H_5)_3Al$–$CF_3CO_2H/H_2SO_4/PPh_3$		C_6 olefins		426, 427, 433
$Ni(ethylene)_2[P(i\text{-}C_3H_7)_3]$–$TiCl_4/WCl_6$		trans C_6 olefins		123
$Ni(propylene)_2(P\text{-}i\text{-}Pr_3)$–$BF_3$	−78 °C	2,3-dimethyl-1-butene (90%)		429
$Ni(C_4H_8)_2$ deposited on PCl_3 treated Al_2O_3–$(C_2H_5)_3Al$	halogenated hydrocarbon/pentane	2-methyl-2-pentene, 4-methyl-2-pentenes	Ni/Al ratio = 1:200	437
$Ni[P(i\text{-}Pr)_3]_2(C_2H_4)/NiP(i\text{-}Pr)_3(C_2H_4)$–$BF_3{\cdot}Et_2O/AlBr_3/HCl$		2,3-dimethylbutenes (36.6%), 2-methylpentenes (59.9%), hexenes (3.5%)		122

TABLE IV (Continued)

cat. system	reactn conditns	products	comments	ref
$Ni[P(OPh)_3]_4$–$AlCl_3/AlBr_3/(C_2H_5)_3Al_2Cl_3$	toluene, chlorobenzene, CH_2Cl_2	*n*-hexene, isohexene	optimum activity at Al/Ni ratio of 5:1 to 7:1; *n*-hexene/isohexene ratio = 3:7	433
$Ni(PPh_3)_3(CH_2)_4$–O_2		2-hexene, 1,2-dimethylcyclobutane		155
$R_4P[(i\text{-}Pr)_3PNiCl_3]$–$(C_2H_5)_3Al_2Cl_3$	toluene	2,3-dimethylbutene, 2-methyl-1-pentene, 4-methyl-1-pentene	increase of temp (−20 to 20 °C) leads to C_9 olefins	436
R(bpy])NiX [R = Ph, *o*-, *m*-, *p*-MeC_6H_4, *o*-Cl-C_6H_4, X = I, Cl, Br]–$EtAlCl_2/Et_2AlCl$	−16 °C	2-methyl-2-pentene, 4-methyl-2-pentene	Al/Ni = 100	438
$Ni(CO)_4$–$AlCl_3$–PPh_3		2-hexene, 4-methyl-2-pentene, 2,3-dimethyl-1-butene	max activity with 2:1 phosphine/$AlCl_3$	440
$NiCl_2$ and $NiCl_2$ treated on a solid carrier–$(C_3H_7)_3Al/(C_2H_5)_3Al_2Cl_3/(Me_2CHCH_2)_3Al_2Cl_3$		2-methyl-2-pentene, 4-methyl-2-pentene, 2-hexene		384
NiX_2 (X = halide) –alR_3	40–80 °C	hexenes (30%), methylpentene (70%)	>95% selectivity to dimerization of selectivity toward *n*-hexenes increased with temp up to 50% at 150 °C	387
nickel salt–$RAlX_2$		2,3-dimethyl-2-butene		539
nickel salt–$RAlX_2$	−20 to 50 °C, 1–5 atm	C_6 olefins		540
$Ni(acac)_2$–$(C_4H_9)_3Al$–BCl_3	hydrocarbons, 20–60 °C, 1800 lb/in.^{2}	2-methyl-1-pentene		541
$Ni(acac)_2$ on SiO_2–Al_2O_3–$(C_2H_5)_3Al_2Cl_3$–PPh_3/PBu_3	145 °F, 3 h	2,3-dimethylbutene (10.9%), 2-methylpentene (66.95%), *n*-hexene (23.13%), nonene, decene		263
Ni oleate–$Al_2R_{6-x}Cl_x$		*n*-hexene, 2-methylpentene		458
Ni naphthenate–$(C_2H_5)_3Al$–PPh_3–2,4,6-$Cl_3C_6H_2OH$		2-methyl-1-pentene, 2-methyl-2-pentene, 4-methyl-1-pentene, 4-methyl-2-pentene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, 1-hexene, *cis*-2-hexene, *trans*-2-butene		542
$Ni(CO)_2(PR_3)_2$–$NbF_5/MoF_6/SbF_5/TaF_5/AsF_5/WF_6/PF_5/VF_5$ (R = Ph, cyclohexyl)	10 °C, 3 h	4-methyl-1-pentene (8.55%), 4-methyl-2-pentene (51%), 2,3-dimethyl-2-butene (2%), 2-methyl-1-pentene (3%), 2-methyl-2-pentene (10%), *n*-hexene (25%)	molar ratio of cat./cocat. is ca. 1:5	543
$Ni(CO)_2(PPh_3)_2$ supported on acidic, calcined Al_2O_3–SiO_2	toluene, 140–160 °F, 70 min	2,3-dimethylbutenes (15%), 2-methylpentenes (53%), hexene (16%), C_9 olefins (15%)		295, 544
$Ni(PPh_3)_4$–BF_3–HF	toluene, 10 °C,	methylpentenes, *n*-hexenes, 2,3-dimethylbutenes	B/Ni = 10:1 yield of dimers vary from 1000 to 4200 mol/g atom of Ni	425
$Ni(PPh_3)_4$ attached to polystyrene–$BF_3{\cdot}OEt_2$–H_2O	0 °C, 1 atm, *n*-hexene/toluene/benzene	methylpentenes (70.3%), 2,3-dimethylbutenes (15.8%), *n*-hexene (13.9%)		428, 545, 546
$NiBr(NO)(PPh_3)$–$(C_2H_5)AlCl_2$	chlorobenzene, 28 psi, 35 °C, 3.5 h	*n*-hexene, 2-methylpentenes, 2,3-dimethylbutenes	44% wt of cocat. is mixed with catalyst	547
$(R_4P)_2(NiCl_4)$–$(C_2H_5)_3Al_2Cl_3$	chlorobenzene, N_2, 0 °C, 100 min, 860 mm propylene	2-methyl-1-pentene (4%), 2-methyl-2-pentene (48%), 4-methyl-1-pentene (1%), 4-methyl-2-pentene (34%), 2,3-dimethylbutenes (5%), *n*-hexenes (8%)	Al/Ni = 40:1, rate of reaction = 49 kg/g of Ni/h; the products consist of dimers = 84%, trimers = 16%	548
$(R_4P)(NiBr_3PR_3)$–$R_{6-x}Al_2Cl_x$	chlorobenzene, 0 °C, 15 min,	*n*-hexene, 2-methylpentenes,	Al/Ni ratio is 30:1	549

	100 mm propylene	2,3-dimethylbutenes		
NiX_2–$AlCl_3$–PR_3		n-hexene, 2-methylpentenes, 2,3-dimethylbutenes		269, 316, 550
$NiBr_2$–$(i\text{-}C_4H_9)_3Al$	65 °C	4-methyl-1-pentene (5.1%), 4-methyl-2-pentene (57.4%), 2-methyl-2-pentene (2.6%), *trans*-2-hexene (26.8%), *cis*-2-hexene (6.5%), 2,3-dimethyl-2-butene (1.6%)		479
$NiCl_2$–$Et_3Al_2Cl_3$–$(i\text{-}C_3H_7)_3P$	o-dichlorobenzene, 1 h, −10 °C	2,3-dimethylbutenes	conversn of propylene = 90–5%; selectivity to the product 76–81%	551
$NiCl_2/NiBr_2$–$(C_2H_5)_2AlCl$–PPh_3/PBu_3		2,3-dimethylbutenes	the product yield increases with increase in basicity of ligands	552
$NiCl_2$–$(C_2H_5)_3Al$–$HCl/(i\text{-}C_3H_7)_3P/$ butadiene	chlorobenzene, 35–40 °C, 15 atm, 9 h	C_6 olefins and C_9 olefins		553
$NiCl_2/NiCl_2$ supported on a solid carrier–$(C_3H_7)_3Al/(C_2H_5)_3Al_2Cl_3/$ $(i\text{-}C_4H_9)_2AlCl$–$AlCl_3$		2-hexenes, 2-methyl-2-pentenes, 4-methyl-2-pentenes	activity of the heterogenized cat. are comparable with that of homogeneous cat.	384, 554
$NiBr_2L_2$–$(C_2H_5)_3Al_2Cl_3$ (L = hexamethylphosphoramide)		n-hexenes (68%), 41-methylpentenes (28%)		315, 555
$NiCl_2L_2$ (L = N,N′-dicyclohexyl-2-(cyclohexylamino)malonamide)	benzene, 30 psig, 30 min	4-methyl-1-pentene, n-hexene, 2,3-dimethylbutenes, 2-ethylbutenes		556
$Ni(acac)_2$–$(C_2H_5)_3Al/(C_2H_5)_2Al(OEt)$		n-hexene (75–80%), 2-methylpentenes (20–25%)		475, 476
$NiCl_2(BuNH_2)_4$–$(C_2H_5)AlCl_2$	chlorobenzene	2-methyl-2-pentene (60%)		557
$NiSO_4(BuNH_2)_4/NiSO_4(py)_4/$ $Ni(ClO_4)_2(py)_4/NiSO_4(RNH_2)_2$–$(CH_3)AlCl_2/(C_2H_5)AlCl_2$ (RNH_2 = lutidine)	−10 to 10 °C, <1 kg/cm^2	2-methyl-2-pentene	Al/Ni = 5–20	527
$Ni(NO_3)_2(py)_4$–$(C_2H_5)AlCl_2$	chlorobenzene, 0 °C, 20 min	2-methyl-2-pentene (51%)		514
NiL_2–$(C_2H_5)AlCl_2$ (L = N,N-dimethyl-2-mercaptoethylamine)	chlorobenzene, 17.5–24.6 °C, 30 min	2-methylpentane (60.3%), hexane (33.1%), 2,3-dimethylbutane (5.2%), 3-methylpentane (1.4%)		557
$Ni(SacSac)PPh_3Cl$–$(C_2H_5)_2AlCl$	toluene, −15 ± 2 °C, 70 min	dimethylbutene (10%), methylpentene (74%), hexene (16%)		559
Ni[poly(4-vinylpyridine)]–$(C_2H_5)AlCl_2/$ $(C_4H_9)_2AlCl$	chlorobenzene	2-methylpentane, n-hexane, 2,3-dimethylbutane, 2-ethylbutane	the cat. offered stable activity over a range of temperatures	137, 262, 560
$[Ni(Me_2SO)_6][NiCl_4]$–$(C_2H_5)_3Al_2Cl_3$	α-chloronaphthalene, 0 °C, 2 min, 13 s	2-methyl-2-pentene (>70%), n-hexenes, 2,3-dimethylbutenes	cat./cocat. mole ratio = 7:50, conversn is 95.5%; selectivity to dimers is 96%	561
$[Ni(R_2SO)_6][MX_4]$–$(C_2H_5)_3Al_2Cl_3$ (R = Me, Et, Ph; M = Fe, Ni, or Co; X = Cl, Br, or I)	1-chloronaphthalene, −2 to 10 °C	hexenes, methylpentenes	90–100% conversns with ~95% yields to C_6 containing up to 75% methylpentenes; addition of moisture increases reaction rate	562
$NiCl_2(Ph_2SO)$–$(C_2H_5)_3Al_2Cl_3$	1-chloronaphthalene, 2.5 min, 0 °C	methylpentenes (75.2%), n-hexene (22.4%), 2,3-dimethylbutenes (2.4%)		563
NiL_2–$(C_2H_5)_2AlCl/(C_2H_5)AlCl_2$–$KOH$ (L = salicylaldimine)	chlorobenzene, 30 min, 20 °C	hexene, nonene		564
NiL_2 supported on bochmite–$(C_2H_5)_3Al_2Cl_3/(C_2H_5)_2AlCl$ (L = n-butylsalicylaldimine)	chlorobenzene, 20 °C	C_6 olefins (72%), C_9 olefin (20%), higher oligomers		326

TABLE IV (Continued)

cat. system	reactn conditns	products	comments	ref
		Copper		
$CuAlCl_4/Cu_2Cl_2$–$(C_2H_5)_2AlCl$	isooctane, 1 atm	*trans*-4-methyl-2-pentene (30.4%), hexenes (27.4%), 2-methyl-2-pentenes (29.9%), *cis*-4-methyl-2-pentene (4.5%), 2-methylpentane (1.3%), 4-methyl-1-pentene (1.0%), 2-methyl-1-pentene (0.6%)		33
		Zinc		
$ZnAl_2Cl_8$–$(C_2H_5)AlCl_2/(C_2H_5)_2AlCl$		*trans*-4-methyl-2-pentene		33
		Zirconium		
$(\eta$-$C_4H_6)_2Zr(dmpe)$		2,3-dimethyl-1-butene		81
(π-allyl)$ZrBr_3$/(benzyl)$ZrBr_3$–$(C_2H_6)_2AlCl/(C_2H_5)AlCl_2$		C_6 olefins, higher α-olefins		332
$Zr(acac)_4$–$(C_2H_5)_3Al_2Cl_3$–PPh_3/PBu_3	155 °F	C_6 olefin		376
		Niobium		
$RR'_nR^2NbAl_m$ [R = cyclopentadienyl, Me-substituted cyclopentadienyl, Me_3C–CH_2; R′ = $PhCH_3$, Me_3C–CH_2; n = 0, 1; R^2 = Me_3CCH, PhCH, $(CH_2)_4$, $CH_2(CHMe)_2CH_2$; A = halogen; m = 1, 2]–$YR^3R^4R^5$ [Y = N, P, As, Sb, Bi; R^3, R^4, R^5 = alkyl, aralkyl, $PhCMe_2CH_2CH_2$, aryl]	decane	C_6 olefin		377
		Rhodium		
$RhCl_3$–HCl		C_6 olefins (major), 2-methyl-2-pentene		160
$RhCl_3 \cdot 3H_2O$	$CHCl_3/PhNO_2$	*n*-hexene (43%), 2-methylpentene (57%)		171, 337
$RhCl_3 \cdot 3H_2O$–$BiPh_3/SbPh_3$		*n*-hexene (15%), 2-methylpentene (85%)		565
$RhCl_3 \cdot 3H_2O$	alcohol	mixed dimers		161
$Rh_2Cl_2(SnCl_3)_4$–HCl	MeOH, 50–70 °C, 1.5–40 atm		use of HCl decreases the pressure required, increases the rate and selectivity of the reaction	339
		Palladium		
$PdCl_2/PdCl_2(BZCN)$	$CHCl_3/CH_2Cl_2$/anisole	hexenes (65–90%)	with $PdCl_2(BZCN)$ isomerization of olefin takes place	171, 173, 337
$PdCl_2$–$(C_2H_5)AlCl_2$–$PPh_3/AsPh_3/SbPh_3$		2-methylpentenes (predominant)		565
$PdCl_2$	acetic acid, HCl	mixed hexenes		336
$Pd(acac)_2$–$(C_2H_5)AlCl_2$–PR_3 (R = Bu, OPh)	CH_2Cl_2	*n*-hexenes (95%)	replacement of PR_3 by $P(OR)_3$ increases the rate but lower selectivity	345, 441
[(π-allyl)PdCl]$_2$–$(C_2H_5)AlCl_2$–$P(OR)_3$		unspecified dimers		239
PdL_2–$(C_2H_5)AlCl_2$	chlorobenzene, 100 psig, 80 °C	hexenes (92.5%)	cat./cocat. mole ratio = 1:50	566
supported $Pd(CN)_2$	100 °C, 775 psig, 2 h	dimers (66%), trimer (11%), oligomers (8%)	linear dimers ~73%	567
		Silver		
$AgAlCl_4$–$(C_2H_5)AlCl_2/(C_2H_5)_2AlCl$		*trans*-4-methyl-2-pentene, 2-methyl-2-pentene		33

		Tantalum		
$(\eta^5\text{-}C_5Me_5)TaCl_2$		*cis*-2,3-dimethyl-1-butene, *trans*-2,3-dimethyl-2-butene		9, 94, 95
$(C_5H_5)Ta(CHCMe_3)Cl_2$		2,3-dimethyl-1-butene	this system is inactive after 20 turnovers	9, 96
$(C_5H_5)Ta(CHCMe_3)Cl_2$	decane, 45 °C, 45 psi	2,3-dimethyl-1-butene (93%)		377
		Tungsten		
WCl_6–$(C_2H_5)_3Al_2Cl_3$–$MeNH_2$/c-$C_5H_{11}NH_2$/$PhNH_2$/*p*-$XC_6H_4NH_2$ (X = Cl, Br, CH_3, etc.)	chlorobenzene, 20 °C, 1 h	2,3-dimethyl-1-butene (64%), 2-methyl-1-pentene (39%)	cat./cocat. mole ratio = 1:10; cat./amine mole ratio = 1:2	379, 380
WCl_6/WBr_5–$(C_2H_5)AlCl_2$–2,4,6-$R_3C_6H_2NH_2$ (R = H, Br, Cl)	chlorobenzene, 60 °C, 1 h	C_6 olefins	conversn of propylene is 39%; selectivity for C_6 olefins is 98%	207
WCl_6–phenols–$(C_2H_5)_3Al_2Cl_3$–$PhNH_2$		2,3-dimethyl-1-butene (53.5%), 2-methyl-1-pentene (37%), 4-methyl-1-pentene (7.7%)	cat./phenol mole ratio = 1:1; conversn of propylene is 94% with selectivity to dimer 99%	381
WCl_6–BzOH–$(C_2H_5)_3Al_2Cl_3$–$PhNH_2$		2,3-dimethyl-1-butene, 2-methyl-1-pentene, 4-methyl-1-pentene	cat./BzOH mole ratio = 1:1; conversn of propylene is 77% with selectivity to dimers is 90%	382
WCl_6–$(RCO)_2CH_2$–$(C_2H_5)_3Al_2Cl_3$–$PhNH_2$ (R = Me, CMe_3, Ph)	chlorobenzene	4-methylpentene (5.3–6.3%), 2,3-dimethyl-1-butene (43–54%), 2-methyl-1-pentene (28–31%)	$WCl_6/(RCO)_2NH_2$ mole ratio = 1:1; conversn of propylene is 69–74% with selectivity to dimers 76–92%	383
		Platinum		
$PtCl_2$–$(C_2H_5)AlCl_2$		*n*-hexene (40%), 2-methylpentene (60%)		565
		Cerium		
$Ce(acac)_3$–$(C_2H_5)_3Al_2Cl_3$–PPh_3	chlorobenzene, 600 psig, 95 °F, 3.5 h	2-methylpentenes and 2,3-dimethylbutenes (78%), *n*-hexenes (22%)	conversion of propylene is 8%	442
$Ce(acac)_3$–$(C_2H_5)_3Al_2Cl_3$–PPh_3	chlorobenzene, 100–125 °C, 150 psig, 60 min	C_6 olefins	yield of dimer is lower in the absence of PPh_3	443
		Thorium		
$Th(NO_3)_4$–$(C_2H_5)_3Al_2Cl_3$–PPh_3	chlorobenzene, 350–500 psig 115–120 °C, 2.5 h	C_6 olefins	yield of dimers is 61%	444
$Th(NO_3)_4$–$(C_2H_5)_3Al_2Cl_3$–PPh_3	chlorobenzene, 115–120 °F, 150–1500 psig, 3 h	2,3-dimethyl-1-butene, 2-methyl-2-pentene	cat./PPh_3 mole ratio = 1:8.5	445

TABLE V. **Representative Kinetic Data for the Dimerization of Propylene**[a]

cat. system	reactn condtns	rate data (T, °C)	remarks	ref
$CrCl_3(py)_3$–$(C_2H_5)AlCl_2$	chlorobenzene/cyclohexane, 100 psig, 1.5 h	1.5 g/(L·min) (50)	data for similar chromium complex given	99
$Co(N_2)(PPh_3)_3$	benzene, 1 atm	1.92×10^{-2} mol^{-1} L·min^{-1} (10)	E_a = 22.9 kcal/mol; $\Delta H^\ddagger$ = 22.3 kcal/mol; $\Delta S^\ddagger$ = 13 cal/(mol·K)	388
$Co(acac)_3$–$HAl(C_2H_5)_2$–PPh_3	methyl–pentenes, 3 bar, $[Ph_3P]/[cat.] = 1$	2.22 g/(L·min) (25)	data for various $[Ph_3P]/[cat.]$ ratios given	25
$NiCl_2$–C_4H_6–$Al(C_2H_5)_3$	chlorobenzene, 15 atm, Al/Ni = 2	140 g/min (35–40)		1
$Ni[Hf(acac)]_2$–i-Bu_3Al	toluene, Al/Ni = 4	1.7 g/(L·min) (80)		50
$(C_6H_5)NiBr(PPh_3)_2$–$BF_3 \cdot OEt_2$–H_2O	CH_2Cl_2, 1 atm, n-hexane, 1 atm	9.6×10^{-3} g/min (0), 0.045 g/min (0)	data in various solvents	289
$Ni(SacSac)PEt_3Cl$–$(C_2H_5)_2AlCl$	toluene, 6 h, chlorobenzene, 6 h	1.3 g/(L·min) (−15), 6.64 g/(L·min) (−15)	rate data for similar nickel complexes given	51
$Ni(acac)_2$–$(C_2H_5)_3Al_2Cl_3$–PPh_3	toluene, 1 atm	6.75×10^{-2} mol^{-1}·L·s^{-1} (−20)	E_a = 13 kcal/mol	415
$R'R_3P[(R_3P)NiCl_3]$(R' = benzyl; R = isopropyl)–$Et_3Al_2Cl_3$	toluene, 860 mm, Al/Ni = 100	356.4 g/(L·min)	data for various Al/Ni ratios	436

[a] Calculated from data available in the literature.

consisting of a transition-metal derivative and an organoaluminum compound. Many mechanisms have been proposed for the dimerization reaction. The most notable among them are Cossee's mechanism, Belov's proposal involving bititanium species, and Schrock's mechanism involving metallacyclopentane. More investigations are in order to get a more decisive picture on the dimerization course. The dimerization of propylene can be complex owing to the possibility of the formation of many products depending on the nature of insertion. It is also observed that apart from transition-metal-based catalysts, studies based on rare-earth elements are scarse. Several industrial processes are known for the dimerization of propylene: however, only pilot plant studies are available for the conversion of ethylene to linear dimers.

Registry No. Ethylene, 74-85-1; propylene, 115-07-1.

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