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).

† 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.)
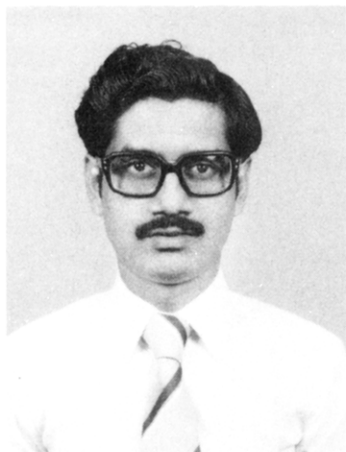
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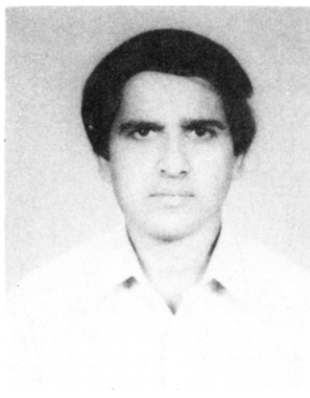
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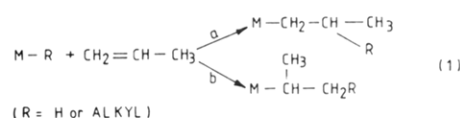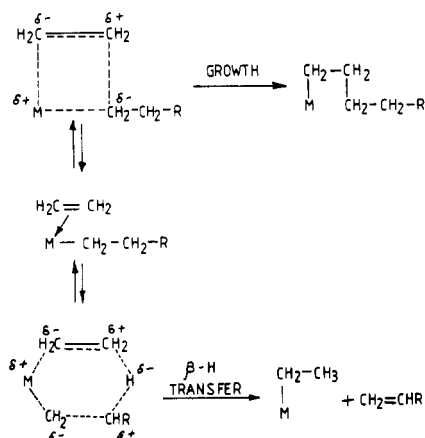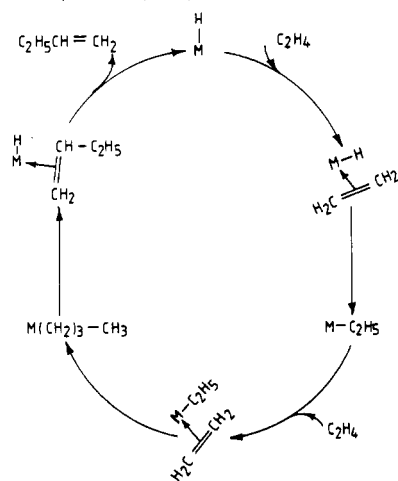
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Coordination of the olefin at the metal hydride center and subsequent insertion of the carbon–carbon double bond of the coordinated olefin into the metal–hydride bond can be related to the initial step of a classical polymerization. The metal–carbon 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.

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

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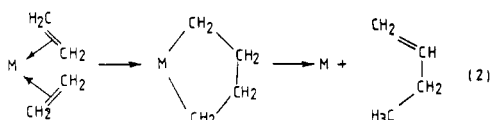
SCHEME I. Chain Growth and β-Hydrogen Transfer from a Metal Alkyl Olefin Complex

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

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

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

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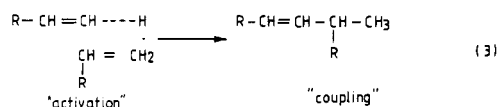
The catalytic cycle for the dimerization of ethylene based on this mechanism is depicted in Scheme II.[14]
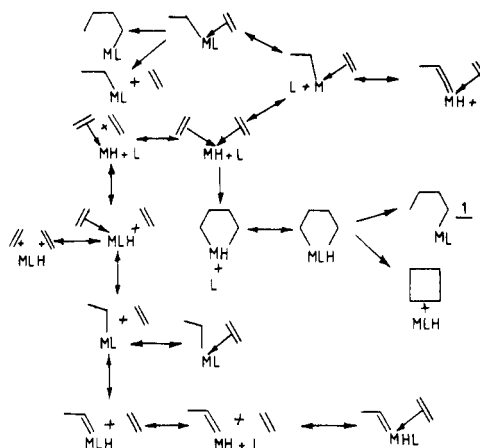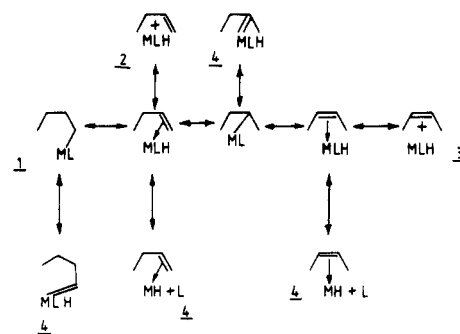
B. Concerted Coupling

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

$$M-CH_2-\underset{R}{\overset{\text{ }}{CH}}-R' + H_2 \longrightarrow M-H + CH_3-\underset{R}{\overset{\text{ }}{CH}}-R' \qquad (4)$$

$$2M \overset{R}{\underset{R'}{<}} \longrightarrow M-M + 2R-R' \qquad (5)$$

$$M-M + H_2 \rightarrow 2M-H$$

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-

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.

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
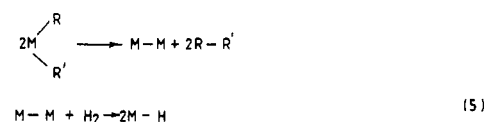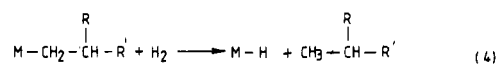
III. Catalytic Dimerization of Ethylene Using Transition-Metal Complexes

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.
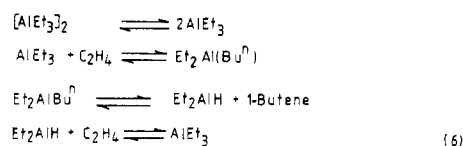
A. Group 11 (IB) Elements

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

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

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]

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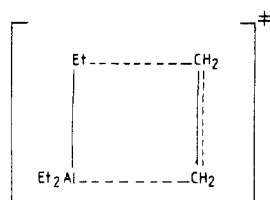
The observed Arrhenius factor of $\sim 10^{6.2}$ $L \cdot mol^{-1}$ s^{-1} is consistent with a molecule–molecule interaction. Moreover, this low value shows that the formation of a loose π-complex cannot be rate determining but the subsequent step leading to formation of a polar, four-centered transition 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 $Ti(O-n-Bu)_4$ 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
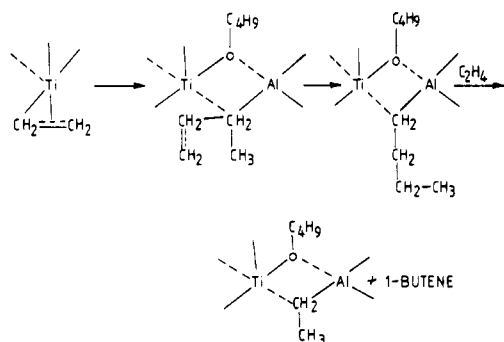
SCHEME VI. Generation of Active Catalyst from the Ti(OCH₃)₄-Al(C₂H₅)₃ System
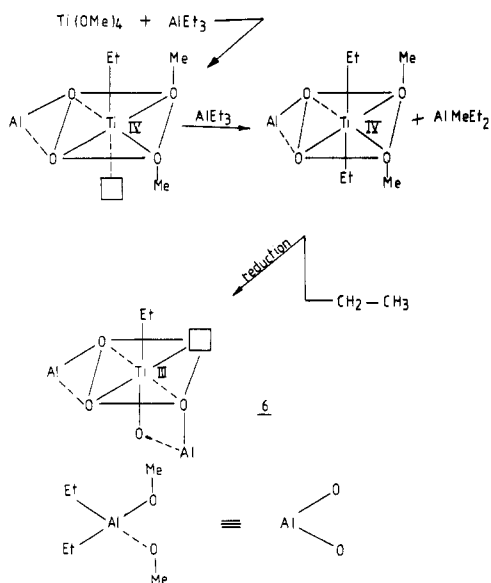
SCHEME VII. Cossee's Mechanism for Dimerization of Ethylene by Ti(OCH₃)₄-Al(C₂H₅)₃
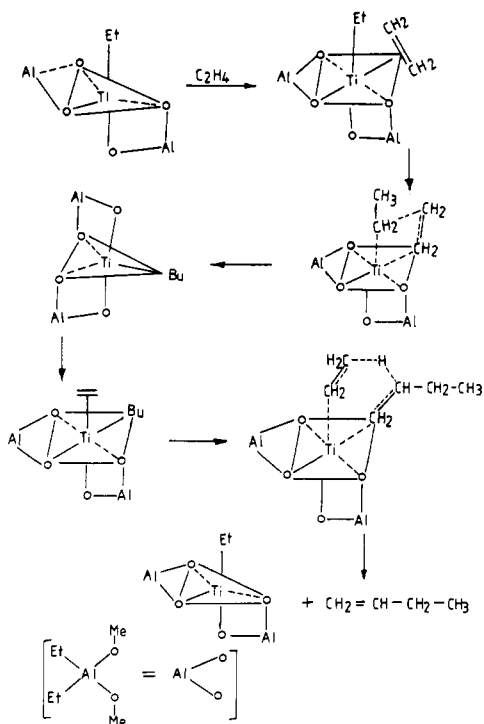
SCHEME VIII. Generation of Bititanium Centers from the Ti(OR)₄-Al(C₂H₅)₃ System
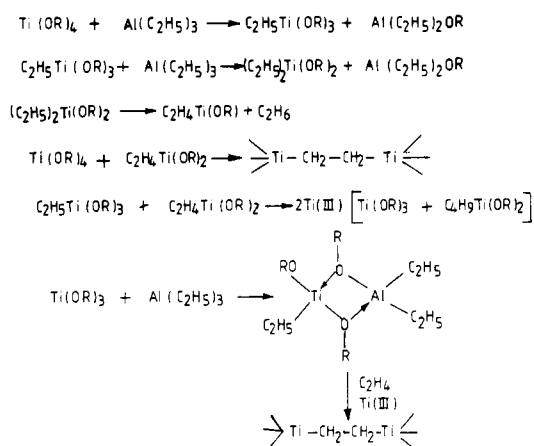
catalyst. Modification of the catalyst Ti(OR)₄-AlR₃ by additions of oxygen allows a 10-20% increase in the yield of 1-butene with simultaneous enhancement of the process selectivity. The quantity of oxygen in the reaction vessel is varied within 0.2:1 to 2:1 with regard to the quantity of alkylaluminum 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 AlEt₃-Ti(O-n-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-Et₃Al systems[58] are summarized in Table I.

Cossee[59] has proposed originally a mechanism for the dimerization of ethylene by the Ti(OMe)₄-AlEt₃ 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-CH₂-CH₂-Ti< groups for the dimerization of ethylene by Ti(O-n-Bu)₄-AlEt₃ 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 AlMe₃ are produced as a result of the recombination of carbeniod intermediates (eq 7). Conversion of carbeniod
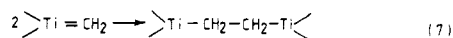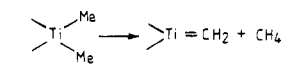
TABLE I. Typical Reaction Conditions for the Dimerization of Ethylene Using Titanium Aryl Oxide and Triethylaluminum

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
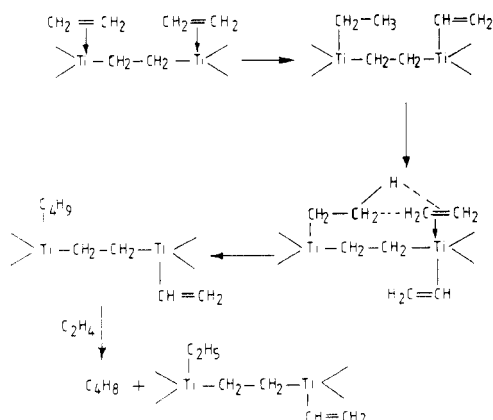
species into metallacyclobutane and similar compounds (7) are more facile[65,66] (eq 8) than the recombination of

carbene species as shown in eq 7 by Belov and co-workers. Thus the proposal is an unusual one and requires further investigation.

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]

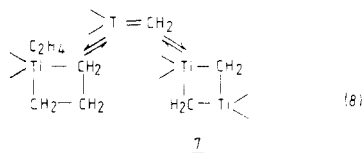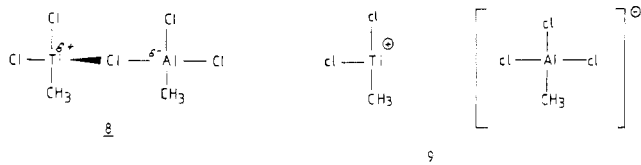The two-component organometallic catalyst MeTiCl$_3$–MeAlCl$_2$,[78] which is distinct from other Ti–Al systems, shows the following order of activity for the dimerization of ethylene in organic solvents: chlorinated hydrocarbons > aromatic hydrocarbons > aliphatic hydrocarbons. It exists as 8 or 9. The selectivity

SCHEME X. Dimerization of Ethylene on the Cationic Part of Complex 9
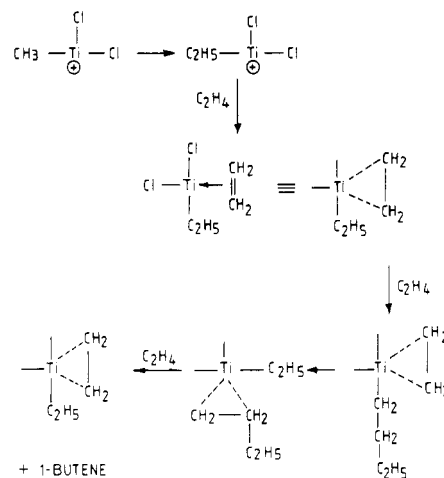
SCHEME XI. Dimerization of Ethylene via a Titanacyclopentane Complex
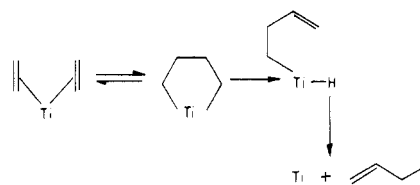
of the catalyst is poor in these solvents. The cationic part of the complex coordinates with the olefin, and the mechanism of the reaction is given in Scheme X.

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 $\rightarrow$ 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 tita-

nium 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 = $\eta^5\text{-}C_5H_5$)
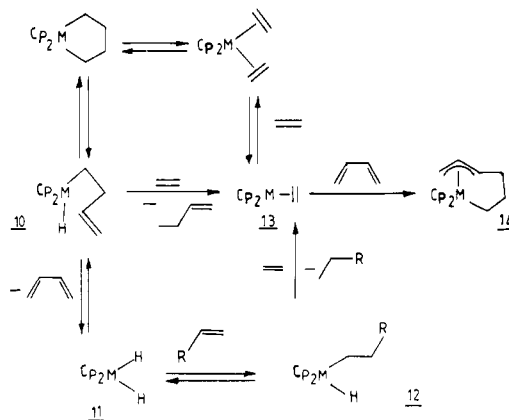
SCHEME XIII. Proposed Mechanism for Ethylene Dimerization by the $Ta(CH_2C[CH_3]_3)_3(CHC[CH_3]_3)$–$2P(CH_3)_3$ System
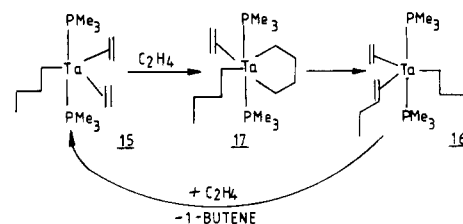
2. Niobium

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 ($\sim 3\%$ 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
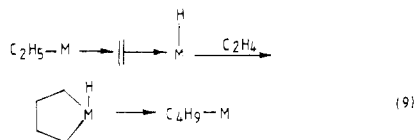
niobium system fails to dimerize ethylene to 1-butene because of its inability to form a metallacyclopentane complex.

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, $[(\pi\text{-}C_6H_6)\text{-}Mo(\pi\text{-}allyl)Cl]_2$,[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

$$CoBr(PPh_3)_3 + BF_3 \cdot OEt_2 \longrightarrow [Co(PPh_3)_3]^+ [BF_3 \cdot Br]^- \qquad (10)$$
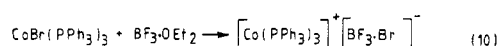
chloride and boron trifluoride etherate show no dimerization activity with cobalt complexes. Addition of triphenylphosphine and water stops the dimerization almost completely.

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 $[Co(C_2H_4)(PPh_3)_3]_2$

$$\left[Co(C_2H_4)(PPh_3)_3 \right]_2 \longrightarrow 2\,Co(C_2H_4)(PPh_3)_3$$

18

19

SCHEME XV. Nickelocene-Catalyzed Dimerization of Ethylene

SCHEME XVI.
(η^3-Cyclopentenyl)(η^5-cyclopentadienyl)nickel-catalyzed Dimerization of Ethylene
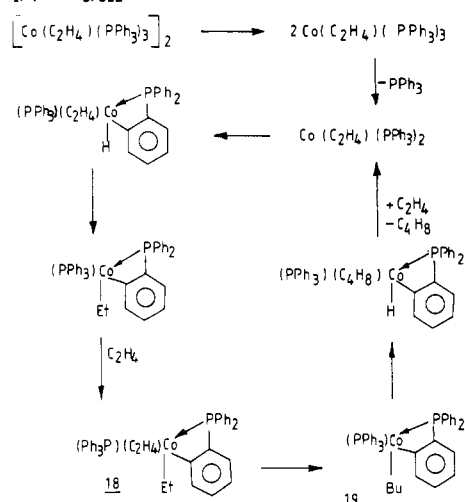
the less expensive of the transition elements. Because of these advantages much research has gone into the study of nickel-catalyzed dimerization.[114-140]

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

17 a

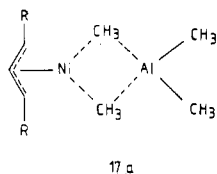and nickel atoms has been demonstrated from these studies. These systems further react with coordinated ethylene molecules in a concerted manner to give butenes.

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(π-allyl)$_2$, or Ni(π-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$_2$Al(OEt) is a weak Lewis acid, and hence the
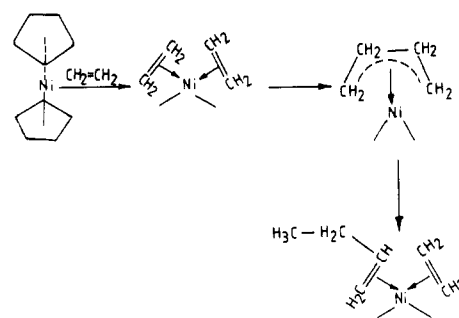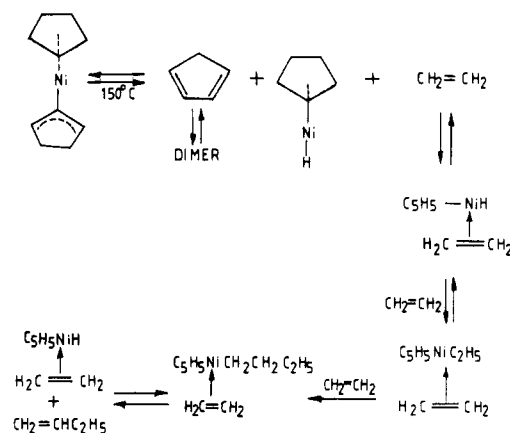
system Ni(acac)$_2$-Et$_2$Al(OEt) is less active. But in the system NiCl$_2$-PR$_3$-AlCl$_3$ the phosphine can play the role of a reducing agent.

The catalytic species formed "in situ" by the reaction of Ni(II) with R$_{6-x}$Al$_2$X$_x$ 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-Ni-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).

(η^5-C$_5$H$_5$)Ni(η^3-C$_5$H$_7$)[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 (η^5-C$_5$H$_5$)Ni(η^3-C$_5$H$_7$) to generate (π-cyclopentadienyl)nickel hydride (Scheme XVI) as a catalytically active intermediate.

SCHEME XVII. Dimerization of Ethylene Catalyzed by Nickelacyclopentane Phosphine Complexes

SCHEME XVIII. Dimerization of Ethylene under the Influence of Rhodium Chloride in Alcoholic Hydrogen Chloride Solutions (S = Cl⁻, H₂O, or Solvent)
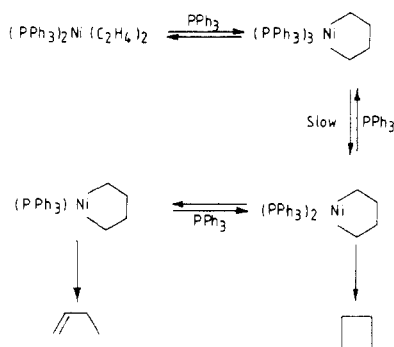
Ozaki and co-workers[152] have reported dimerization of ethylene catalyzed by bis(triphenylphosphine)(pentachlorophenyl)chloronickel(II) activated with silver salts like $AgClO_4$ or $AgBF_4$. The activity is enhanced by adding a catalytic amount of PPh_3 ($PPh_3/AgClO_4$ ≤ 1). An excess of PPh_3 ($PPh_3/AgClO_4$ ≤ 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 $BF_3·OEt_2$ 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-
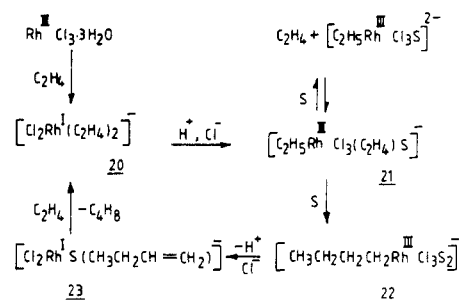
$(n\text{-}Bu)_3$ for the dimerization of ethylene.[158] The reaction is second order with respect to monomer and first order with respect to nickel but is of a complex order with respect to aluminum compounds. The overall activation energy lies between 7 and 9 kcal/mol. Kinetics of ethylene dimerization in the presence of heterogenized (π-allyl)nickel complexes is also investigated.[159]

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

$$\left[Cl_3(C_2H_4)RhCH_2CH_2CH_2CH_2\right]^{2-} \xrightarrow[\text{Solvent}]{H^+} \left[Cl_3(C_2H_4)Rh(C_4H_9)S\right]^{-} \quad (11)$$
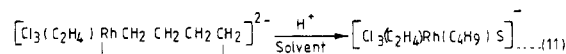
$$\frac{d[C_4H_8]}{dt} = k[C_2H_4][\overset{+}{H}][Cl^-][Rh] \quad (12)$$

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.

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

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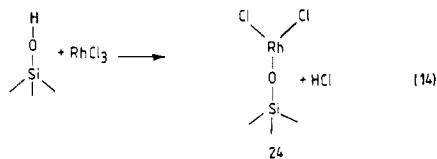
The high dimerization activity is due to the ligand effect of Si–O– on rhodium. Activation energy for the dimerization is calculated as 7 kcal/mol which is about half of that obtained by using the homogeneous catalysts.

$[Rh(SnCl_3)_2Cl_4]^{3-}$ 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.

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

SCHEME XIX. Dimerization of Ethylene Catalyzed by PdCl₂ in the Presence of Hydrogen Chloride
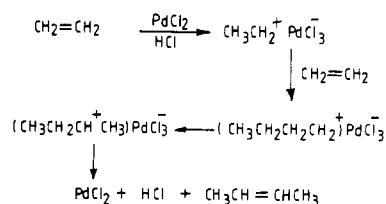
SCHEME XX. Dimerization of Ethylene by PdCl₂
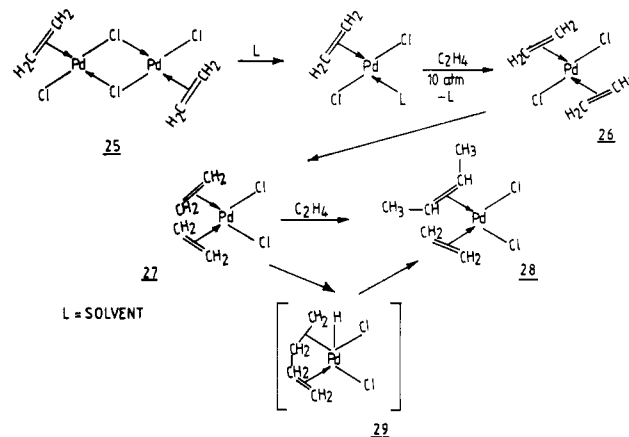
L = SOLVENT

$PdCl_2$, 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$_m$Cl$_n$L$_2$-catalyzed Dimerization of Ethylene
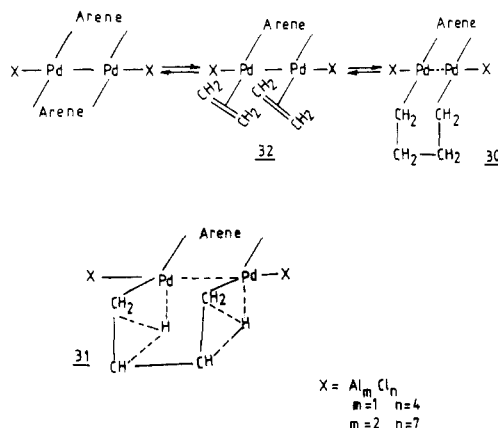
The dimerization of ethylene by Pd(BzCN)$_2$Cl$_2$ has been reported by Barlow and Bryant.[173] Dimerization and the accompanied isotopic exchange of ethylene have been studied with Pd(BzCN)$_2$Cl$_2$ in benzene.[174] Both the reactions take place after an induction period, the extent of which is reduced 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$_m$Cl$_{n-2}$ (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$_2$SO)$_2$[177-179] and K$^+$PdCl$_3^-$(Me$_2$SO) 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$_3$·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$_2$Cl$_2$ in the presence of Et$_2$AlCl[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$_2$Cl$_8$ with EtAlCl$_2$ or Et$_2$AlCl 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.

$$CH_3-CH_2CH_2Al\big\langle \cdot C_3H_6 \longrightarrow CH_2-CH_2-CH_2$$
$$CH_3-CH-CH_2Al\big\langle \quad (15)$$

$$CH_3-CH_2-CH_2$$
$$CH_3-CH-CH_2-Al\big\langle + C_3H_6 \longrightarrow$$

$$CH_3-CH_2-CH_2 + CH_3-CH_2-CH_2-Al\big\langle$$
$$CH_3-C=CH_2 \qquad (16)$$
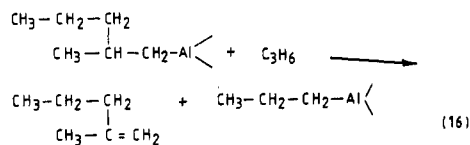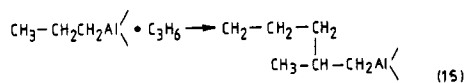
If the propylene dimer 2-methyl-1-pentene is taken out of the reaction mixture, the mechanism of the process becomes catalytic and a small amount of the alkylaluminum compound will be sufficient to dimerize the propylene.[361-363] In the dimerization of propylene at high temperatures and pressures using 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%). $(\eta$-$C_4H_6)_2$Ti-
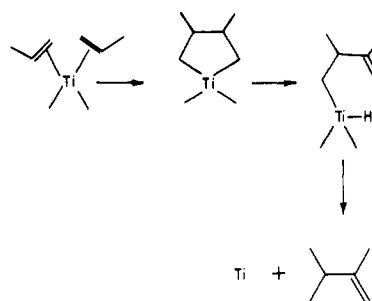
(dmpe) catalyzes the dimerization of propylene to 2,3-dimethyl-1-butene, suggesting metallacycle formation (Scheme XXII) as an intermediate in the reaction.[81]

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

$(\eta$-$C_4H_6)_2$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	$R_oAl/Ti(OR)_4 < 10$; high selectivity to 1-butene	44, 188, 189, 190, 191
$Ti(OR)_4$-R_3Al		1-butene, 2-butenes		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

Catalyst	Conditions	Products	Notes	Ref.
TiCl₄-(CH₃)₃Al₂Cl₃				
Ti(O-n-Bu)₄-[(CH₃)₂CH]₃Al	n-heptane, -100 °C	1-butene, 2-butenes, polymer	halogenated hydrocarbons > aromatic hydrocarbons > aliphatic hydrocarbons	204
C_pTiCl₂-amalgams of alkali metals	cyclohexane, ethylene = 500 psi, 75 °C, 26 min	1-butene (80-88%), 1-hexene (12-20%)		80, 205, 206, 207
C_pTiCl₂-(C₂H₅)₃Al-Ti(O-n-Bu)₄	5 kg/cm², 30-32 °C, 4-5 h	1-butene (88-95%)		54
(π-C₄H₆)₂Ti(dmpe)	heptane/decane/toluene	1-butene, cis-2-butene, 3-methyl-1-pentene, 2-methyl-1-pentene		81
Ti (cyclopentadienyl)	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-n-Bu)₄-R₃Al	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-n-Bu)₄-(C₂H₅)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-R₃Al	0.2-2.0 equivalent of oxygen based on cocatalyst; organic solvent	1-butene		215
Ti(OBu)₄-(C₂H₅)₃Al-CH₃OCH₂CH₂OCH₃	pentane	1-butene, mixture of hexenes		216
Ti(OR)₄-R₃Al-C₄H₉OH/C₆H₅OH		1-butene		217
Ti(O-n-Bu)₄-(C₂H₅)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-R₃Al-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 = C₁₋₆ 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-R₃Al-C_pTiCl₂/o-phenylenediamine	ethyl chloride, C₂H₄ = 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(C₂H₅)-(C₂H₅)₃Al; (PhCH₂O)₄Ti-(C₂H₅)₃Al; Ti(OBu)₄-HAl(i-Bu)₂	heptane/decane/toluene/ether/THF	1-butene (88-95%)		54
Ti(OR)₄-H₂AlNMe₂/H₂AlNBu₂/HAlClNBu₂	toluene, 65-70 °C, 20-60 atm, 3 h	1-butene (94%)		225
Ti(OR)₄-(C₂H₅)₃Al/AlH(i-C₄H₉)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(OC₂H₅)₂(acac)₂-(C₂H₅)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(CH₃)₂]₄-(C₂H₅)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
(π-C₅Me₅)Ti(OR)₃-(C₂H₅)₃Al	isopropylcyclohexane, 30 °C, 3 h	1-butene (>90.9%), hexenes (7.9%), butane (1%)	Al/Ti ratio = 3:1	228
(OR)₃Ti(acac)-R₃Al-R₂HAl	heptane, 30 °C, 2 h, ethylene = 5 kg/cm²	1-butene		229
L₂TiH₃ (L = Me₂PCH₂CH₂PMe₂)		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)
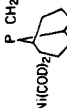
cat.	reactn condtn	products	comments	ref
		Vanadium		
VCl_3-$(i$-$C_4H_9)_3Al_2Cl_3$	heptane, 30 min, 60 °C, 3 atm	1-butene (7%), trans-2-butene, (47%), cis-2-butene, (41%), hexenes (3%), octene (0.6%), higher olefins (1.4%)		92
$VO(O$-i-$Pr)_3$-$(C_2H_5)_3Al$	heptane, 7.12 atm, 90 °C, 160 min	1-butene	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 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/cm², 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/cm², 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/cm², 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
$Co(acac)_3$-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%	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	activity is 60 g/mol of Co.hr	105
$CoH(N_2)(PPh_3)_3$	25 °C	2-butenes (95–99%)		109
$CoX(PPh_3)_3$-BF_3·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

catalyst	conditions	products	comments	ref
CoBr₂(PPh₃)₂–(C₂H₅)AlCl₂	o-chlorotoluene; toluene, 30 °C, 2 h	1-butene, 2-butene	chlorobenzene > o-chlorotoluene, B–Co ratio is 1	237
[Co(C₂H₄)(PPh₃)₃]₂	benzene, 20 °C, 1 atm	trans-2-butene (63.0%), cis-2-butene (24.5%), 1-butene (1.5%), hexenes (10%)	1-butene/2-butene ratio = 1:20; E_a = 12.4 kcal/mol ΔH = 11.8 kcal/mol ΔS = 16 cal/(mol·K)	112
bochmite/bayerite/γ-Al₂O₃ impregnated with bis(n-butylsalicylideniminato)-cobalt(II)–(C₂H₅)₃Al₂Cl₃	chlorobenzene	butenes, hexenes, octenes		238
		Nickel		
(π-allyl)nickel halide–R₃Al	toluene, 8 atm, 55 °C, 3 h	2-butenes (major), 1-butene		239, 240
(π-allyl)nickel halide–TiCl₄/VOCl₃		1-butene (21%), trans-2-butene (52%), cis-2-butene (27%), hexenes, polymer (minor)		241, 242
(π-allyl)nickel complex–AlCl₃ alkylbenzene complex		butenes (major), hexenes, polymer		243
(π-allyl)nickel halide–AlCl₃/ AlBr₃/AlRCl₂–PR₃		butenes		1, 118, 134, 143, 147, 148, 244, 245, 247
(π-allyl)nickel halide supported on Al₂O₃–(C₂H₅)₃Al₂Cl₃		1-butene, 2-butenes		159, 248
(π-C₅H₅)₂Ni	200 °C, 600 psi	2-butenes (major), 1-butene (minor)	ethylene conversn is 70–90%	2, 152, 153
(π-C₅H₅)(π-C₃H₇)Ni	145–150 °C	1-butenes 82–90%	ethylene conversn is 90%	126
(π-C₅H₅)(π-C₃H₇)Ni	benzene, 150 °C, 30 min	butenes (78%), hexene (15%), and octene (3%)		249
(π-C₅H₅)(π-C₅H₇)Ni supported on SiO₂–Al₂O₃	heptane, 50–75 °C, 1 h	butenes, hexenes, octenes	ethylene conversn is 84%	250
(π-C₅H₅)(π-C₅H₇)Ni supported on SiO₂–Al₂O₃	14–21 atm, 50–60 °C, 1 h	C₄⁻ (47%), C₆⁻ (27%), C₈⁻ (9%), C₁₀⁻ (7%), C₁₂⁻–C₂₂⁻ (10%)	1-butene in C₄⁻ is 95%	251
Ni(acac)₂–Rₓ–Al₂Clₓ–PPh₃ (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–(C₂H₅)₃Al–BCl₃	heptane, 20 min, 60 °C, 15 kg/cm²	butenes		258
Ni(acac)₂–(C₂H₅)₂AlCl–PPh₃	toluene, 50 °C	1-butene, 2-butenes	[Ni]/[Al]/[PPh₃] = 1:9:3; amount of butenes is 48.6%; 1-butene in C₄⁻ is 5%; 2-butene is 95%	235
Ni(acac)₂–(C₂H₅)₃Al₂Cl₃–PR₃ (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–(C₂H₅)₃Al–(C₂H₅O)₃Al–PhC≡CH	xylene, 110 °C, 60 atm, 5 h	1-butene (86%)		259
Ni(acac)₂–(C₂H₅)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–BF₃·OEt₂/(i-Bu)₃Al		2-butenes (98%), 3-methylpentenes, 1-butene		119
Ni(acac)₂ supported on SiO₂–Al₂O₃ or Al₂O₃–(C₂H₅)₂AlCl–PPh₃		butenes		261, 262, 263
Ni(acac)₂ supported on inorganic oxide–(CH₃)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-C₄H₉)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-C₃H₇)₂–PPh₃	20 °C, 2.5 atm	1-butene (80%), cis-2-butene (9%), trans-2-butene (11%)		266
nickel fluoroacetylacetonate–(C₂H₅)₂Al(OC₂H₅)	halohydrocarbons, −10 to 100 °C	butenes		267
nickel salts–haloorganoaluminums–B(OR)₃		2-butenes		268
NiCl₂-AlCl₃-PR₃/amine	chlorobenzene, 20 °C	butenes (78%), C₆ olefins (20%)		269, 270
NiCl₂ or Ni(OAc)₂-NaBH₄-phosphinobenzoic acid	HO(CH₂)ₓOH	C₄ and higher olefins (8–34%)		271
NiCl₂·6H₂O-Ph₂PCH₂CO₂K-NaBH₄	HO(CH₂)₄OH, 75 °C, 750 psig	butenes (45%), C₆-C₁₀ olefins (48%), C₁₂-C₂₀ olefins (6.3%)	Ni/ligand = 1; NaBH₄/Ni = 2; activity = 2350 g/g of Ni/h	272
NiX₂-Ph₂PCH₂CO₂H-NaBH₄-PPh₃	HO(CH₂)ₓOH, 100 °C, 40 atm	C₄⁻-C₈⁻ (41%), C₁₀⁻-C₁₈⁻ (40.5%), C₂₀⁻ (18.5%)		273–275
polymeric gel immobilized NiCl₂/Ni(NO₃)₂-(C₂H₅)AlCl₂		butenes		276
trans-(PPh₃)₂Ni(o-aryl)Br	chlorobenzene/CH₂Cl₂, 0 °C, 1 atm	butenes		117, 277
NiBr(L)(PPh₃)₂-BF₃·OEt₂ (L = Br, mesityl, naphthyl, o-tolyl)		butenes	rate of dimerization increases in the order Br << mesityl < naphthyl < o-tolyl	114, 120, 127
(C₆Cl₅)Ni(PPh₃)₂Cl-AgClO₄-PPh₃	bromobenzene, 0 °C, 1 atm	butenes	selectivity is 80–100%	152
(C₆H₅)Ni(PPh₃)₂Br-AgClO₄		butenes	max activity for AgClO₄/nickel complex = 2	154, 278
(o-tolyl)Ni(PPh₃)₂Br/ (1-naphthyl)Ni(PPh₃)₂Br/ (mesityl)Ni(PPh₃)₂Br-BF₃·OEt₂	CH₂Cl₂, 0 °C, 5 min	butenes		279
NiX₂(PR₄)₂-Al₂R₆₋ₓClₓ-haloalkane (x = 2, 3, or 4)		butenes	[Ni]/[Al] = 1:20–85; haloalkane/Al = 1–18:1	280, 281, 282
NiCl₂(PBu₃)₂-(C₂H₅)₂AlCl-C₃-C₁₂ alkyl halide		butenes, 2-butenes, hexenes, 3-methylpentenes		283
LNiPh₃P=CHBz		α-olefins		284
NiX₂-PR₃-R'ₙAlX₃₋ₙ supported on solid carrier (X = halogen, R = alkyl, cycloalkyl, R' = R, n = 1, 3)		butenes		285
NiCl₂(PBu₃)₂ supported on SiO₂-Al₂O₃-(C₂H₅)₂AlCl	300 °F, 2 h	1-butene (12%), 2-butene (88%)	selectivity to butene is 68–73%	286
NiX₂-PR₃/pyridine/bipyridyl-RAlX₂ (R = alkyl)	chlorobenzene	butenes		287
NiX₂(PR₃)₂-Al₂R₆₋ₓClₓ (x = 2, 3, or 4)	hexane, 0 °C, 1 atm, toluene	1-butene, 2-butenes, hexenes, 3-methylpentenes		150, 158
HNiCl[P(i-PrO)₃]-(C₂H₅)₃Al₂Cl₃		butenes		124
Ph₃PNi⟨ ⟩ -LiCl	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(PPh₃)₄-AlCl₃/AlBr₃	chlorobenzene, 50 °C	1-butene (4.4%), trans-2-butene (68.5%), cis-2-butene (27%)		288
Ni(PPh₃)₄ supported on polymer, BF₃·OEt₂		butenes		121, 180, 289
polystyrene supported Ni(PPh₃)₄-BF₃·OEt₂-(C₂H₅)₃Al₂Cl₃-PPh₃		butenes, 3-methyl-pentenes		136, 156, 157
Ni(PCl₃)₄-AlBr₃-LiBu	chlorobenzene, argon, 1 atm, 20 °C, 30 min	1-butene and cis- and trans-2-butenes		116, 269, 290, 291

catalyst	conditions	products	remarks	ref
Ni(PPh₃)₂(NO)₂–(C₂H₅)AlCl₂		butenes, hexenes, octene		292
Ni(CO)₄–PPh₃–(C₂H₅)₃Al₂Cl₃ supported on Al₂O₃		C₄ hydrocarbons		293
Ni(CO)₄–(C₂H₅)₂AlCl–(C₂H₅)AlCl₂–PPh₃	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(PR₃)₄₋ₓ–Al₂R₆₋ₓClₓ (x = 2)		butenes	cat./activator mole ratio is 8.736:1	290
Ni(CO)₂(PPh₃)₂ supported on Al₂O₃–SiO₂–(C₂H₅)ₓAlCl₃₋ₙ (n = 1, 2)	aliphatic or aromatic hydrocarbon 20°–80° C, 2–20 atm	butenes		295, 296
Ni(PR₃)₂(ethylene)–AlCl₃		butenes		297
Ni(ethylene)₃–BF₃–OEt₂–AlCl₃		butenes	maximum activity with BF₃/Ni mole ratio = 3 and AlCl₃/Ni mole ratio = 4	131
Ni(ethylene)₂(i-PPr₃)/Ni(ethylene)-(i-PPr₃)₂–BF₃–OEt₂–AlBr₃		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)₂Ni(i-PPr₃)–BF₃		butenes		129
NiL₂–(C₂H₅)AlCl₂ (L = picoline)	chlorobenzene, 80–100 psig, 180 °F, 12 min	butene (59%), hexene (35.7%), octene (6.9%)		292, 298
NiL₂–(C₂H₅)₂AlCl (L = o-phenylenediamine)	10–30 °C, 5–20 atm	butenes		299
NiCl₂(3-picoline)₂ supported on SiO₂–Al₂O₃–(C₂H₅)₂AlCl		butenes		286
Ni(S₂CNR₂)₂–(C₂H₅)AlCl₂ (R = butyl)	chlorobenzene	butenes, hexenes, octene		292
Ni(π-L)₂X₂–Al₂R₆₋ₓClₓ–PR₃ (x = 2, 3, or 4) (L = tetramethyl-cyclobutadiene)	1 atm, 1 h, 20 °C	C₆ olefins (17%), 1-butene (78%)		150, 158, 295, 300–305
Ni(COD)₂–CF₃COCH₂COCF₃	toluene	butenes	mole ratio of cat. to additive is 0.5:1–2:1	306
Ni(COD)₂–CF₃CO₂H	toluene, 10 h, 25 °C, 500 psi	butenes, higher α-olefins	32 g of oligomers/g of cat./hv	307, 308
Ni(COD)₂–Ph₂PCH₂CO₂H	benzene, 75 °C, 550 psig, 4 h	higher olefins, C₄ to C₂₂ olefins		309
Ni(COD)₂–Ph₂PCH₂CH₂COOH	toluene, 25 °C, 50 bar	C₄–C₂₄ olefins	linearity (99%), α-olefins (99%)	310, 311, 312
Ni(COD)₂–Ph₂PCH₂CH₂COOH supported on Al₂O₃–SiO₂	50 °C, 20 bar, 3 s	C₄–C₂₀ olefins	C₄ 100% linear and 50–90% α-olefins, C₆–C₂₀ 80% linear and 48% α-olefins	310
Ni(COD)₂–PPh₃–Ph₃P=CHCOPh	toluene, 50 °C, 50 bar	C₄–C₃₀ olefins	linearity (99%) and α-olefins (98%)	284, 313
Ni(COD)₂ [P CH₂COOH]	aromatic solvents	α-olefins (99%)	activity is 6000 mol of ethylene/mol of complex	260, 314
NiX₂L₂–Al₂R₆₋ₓClₓ (L = hexamethylphosphoramide, x = 2, 3, or 4)		butenes		315
NiBr₂/NiCl₂–phosphoric tris(diamide)–AlR₃/AlRX₂		butenes, hexenes		316
Ni oleate–(i-C₄H₉)₂AlCl–(t-Bu)C₆H₄Me/oxygen	n-heptane, 1 atm; 30 °C, argon	butenes, hexenes	Al/Ni ratio = 4:6	105, 317, 318
Ni oleate–(C₂H₅)₃Al₂Cl₃–PPh₃	tert-butyltoluene, 20 °C, 3 h	butenes (80%)	ethylene conversn is 48%; Ni/PPh₃ ratio = 1:2	319
Ni palmitate–(C₂H₅)₃Al–PhC≡CH	110–130 °C, 40 atm, 200 h	1-butene	selectivity is high	320, 321, 322
Ni diisopropylsalicylate–Al₂R₆₋ₓClₓ (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(RCO₂)₂–RₘAlX₃₋ₘ–PX₃ (R = alkyl, aryl; m = 1, 2; X = halogen)	–50 °C to +150 °C, 25 atm	butenes		324, 325
bochmite/γ-Al₂O₃ impregnated with	chlorobenzene	butenes, hexenes, octenes		326
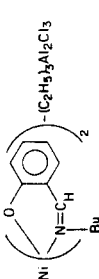
TABLE II (Continued)

cat.	reactn condtn	products	comments	ref
(structure: bis-aldimine Ni complex) $-(C_2H_5)_3Al_2Cl_3$; (structure: naphthyl imine Ni complex)				
group VIII metal halides (R = H, Me, Cl; R = $(CH_2)_2NR^2R^3$, R^3 = R^3 = H, alkyl)	0 °C, 20 min	butenes, hexenes		327
$NiMe_2SO)_6\cdot NiCl_4-(C_2H_5)_3Al_2Cl_3/(C_2H_5)AlCl_2$	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
$Zr(O\text{-}i\text{-}Pr)_4-Al_2Cl_3(C_2H_5)_3$	heptane, 80 °C	C_4, C_6, C_8, and higher α-olefins	Zr/Al/P ratio = 1:10–25:1–3	88
$Zr(O\text{-}n\text{-}Bu)_2(OC_6H_4Cl\text{-}4)_2-PPh_3-(C_2H_5)_2AlCl$	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
$Zr(OR)_4-R_xAlX_{3-x}-PBu_3$ (π-allyl)$ZrBr_3/$ $C_6H_5CH_2ZrBr_3-(C_2H_5)_2AlCl/(C_2H_5)AlCl_2$	organic solvents	1-butene		87
		C_4 and higher olefins		332
L_2ZrH_3 (L = $Me_2PCH_2-CH_2PMe_2$)		butenes		89
(structure: Cp_2Zr cyclopentane)	toluene, 60 °C, 1 atm	n-butane, 1-butene, ethane		90
$Zr(benzyl)_4-(C_2H_5)_3Al_2Cl_3$ (η-$C_4H_6)_2Zr(dmpe)$ (C_4H_6 = 1,3-butadiene, dmpe = $Me_2PCH_2CH_2PMe_2$)	toluene, 40–80 °C	α-olefins		20
		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				
$[(\pi\text{-}C_6H_6)Mo(\pi\text{-}L)Cl]_2-(C_2H_5)AlCl_2$	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

Catalyst	Conditions	Products	Comments	Ref.
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
$(\pi\text{-}C_5H_5)Rh(C_2H_4)_2$	xylene	1-butene, 2-butenes		162
$[Rh(CO)_2Cl]_2$ bonded on SiO_2 or silica gel or Al_2O_3 or zeolite by use of silane derivatives		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		2-butenes, 1-butene		343
$PdCl_2$–$CH_3CH(NO_2)CH_3$	benzene, 18 h, 75 °C, 750 psig	butenes (96.7%), hexene (0.7%), nitropropane (1%)	conversn of ethylene is 80%	344
$PdCl_2$	1 atm, 40–50 °C, 5 h	2-butenes, 1-butene		168, 170–172
$PdCl_2$(ethylene)	halogenated hydrocarbon/RNO_2	butenes		337
Pd_2Cl_4(ethylene)$_2$	dioxane/benzene	butenes		169, 345
$[(\pi\text{-methylallyl})PdCl]_2$–$AgF_4$–$PBu_3$	hexane	butenes, hexenes (≤25%)		346
polymer supported $Pd(PPh_3)_4$–BF_3OEt_2	dibutylphthalate, benzene	butenes		180
$Pd(CN)_2$/PdF_2/$PdBr_2$/PdI_2/$Pd(NO_3)_2$		butenes		6
$Pd(BzCN)_2Cl_2$		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
$[(\eta\text{-arene})PdAl_mCl_n]_2$ (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); $CpTaCl_2(C_4H_6)$ (Cp = cyclopentadienyl anion; C_4H_8 = butadiene)	40 psig	butenes		89
		1-butene with 2-butenes (~3%)		347, 348
$(CH_3CMe_3)_3Ta(CHCMe_3)_3$–$PMe_3$	pentane, 25 °C	1-butene		9, 94, 95, 97, 98
Tungsten				
WCl_4 [arene–amine structure: HN, CH_3, H_3C] –$(C_2H_5)_2AlCl$	benzene, 40 °C	butene (98%)	conversn 84000 mol/mol of tungsten/h	349
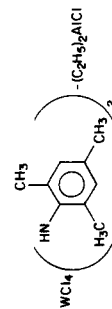
TABLE II (Continued)

cat.	reactn condtn	products	comments	ref
WCl6-(C2H5)2AlCl-2,6-(CH3)2-C6H3NH2	chlorobenzene, 1 h, 40 °C, 27 atm	1-butene (92%)		103
IrCl3	ethyl alcohol	*Iridium* 2-butene (95-99%), 1-butene (1-5%)		161
Pt(PPh3)4 supported on polymer-BF3·OEt2	hexane	*Platinum* butenes		180

TABLE III. Representative Kinetic Data for the Dimerization of Ethylene

cat. system	reactn conditions	rate data, (T, °C)	remarks	ref
Al(C2H5)3	416.7 torr	1.038×10^{-2} mol^{-1}·L·s^{-1} (167)	rate constants at other temp. and pressures given	35
Al(C2H5)3	n-decane, 9-120 psi	0.10 mol^{-1}·L·min^{-1} (100)		52
Ti(n-C4H9O)4-AlR3 (R = CH3, C2H5, n-C4H9)	diethyl or dibutyl ether	20 g/(L·min) (60)	E_a = 15 kcal/mol	67
Ti(n-C4H9O)4-Al(C2H5)3	pentane-dioxan, 1.5 MPa	4.17 g/(L·min) (50)		197
Ti(i-C3H7O)4-Al(C2H5)3	heptane, 7.12 atm, Al/M = 5.6	1.3 g/(L·min) (90)		47
Ti(acac)2Cl2-Al(C2H5)3	heptane, 7.12 atm, Al/M = 4.9	0.18 g/(L·min) (90)		47
Ti(acac)2(OC2H5)2-Al(C2H5)3	heptane, 7.12 atm, Al/M = 6.1	0.08 g/(L·min) (90)		47
Ti(OC6H4CH3)4-Al(C2H5)3	heptane, 7.12 atm, Al/M = 3.7	1.3 g/(L·min) (90)		47
Ti(OC6H5)4-Al(C2H5)3	heptane, 15 kg/(cm²·g), Al/Ti = 3.0	0.5 g/min (40)		58
Ti(OC6H4CH3)4-Al(C2H5)3	heptane, 15 kg/(cm²·g), Al/Ti = 3.0	0.5 g/min (40)		58
Ti(OC6H4Am)4-Al(C2H5)3-P(OPr)3	heptane, 15 kg/(cm²·g), P/Ti = 4.0	1.31 g/min (60)		58
Ti(OC4H9)-Al-i-Bu3	decane, 1 bar, Al/Ti = 4.5	1.125 g/(L·min) (20)		64
Ti(OC4H9)4-Al(C2H5)3	heptane, 4 atm, Al/Ti = 10	0.243 g/(L·min) (20)		62
Ti(OC4H9)4-Al(C2H5)3	heptane, 10 atm, Al-Ti = 7.5	0.25 g/min (20)	rates in other solvents given	62
Ti(OC4H9)4-Al(CH3)3	heptane, 10 atm, Al/Ti = 7.5	0.18 g/min (20)		62
Ti(OC4H9)4-Al(i-Pr)3	heptane, 10 atm, Al/Ti = 7.5	0.09 g/min (20)		62
Ti(O-n-C4H9)4-Al(C2H5)3	toluene, 10 atm, Al/Ti = 10	0.77 g/min (20)		62
Ti(OC4H9)4-Al(C2H5)3	heptane, 460 torr, Al/Ti = 10	3.5 g/(L·min) (22)	rates for other alkoxides given	63
Ti(OC4H5)4-Al(C4H5)3	n-decane, 2.7 atm, 2 h	1.83 g/(L·min) (20)		222
Ti(OC4H9)4-Al(C4H5)3-m-phenylenediamine	n-heptane, 3 atm, 280 min	1.57 g/(L·min) (20)		222
Ti(OC4H9)4-Al(i-Bu)2H	diethyl ether, 9.3 atm, 109 min	6.5 g/(L·min) (60)		222
WCl6-2,6-dimethylaniline-(C2H5)2AlCl	benzene, 1 h, 27 atm	0.85 mol/(L·min) (40)		349
[Co(C2H4)(PPh3)3]2	benzene, 1 atm	6.59 mol^{-1}·L·min^{-1} (10)		112
Ni(C6H5)Br(PPh3)2-BF3·OEt2	CH2Cl2, 1 atm	0.05 g/min (0)		289
V(O-C3H7)4-Al(C2H5)3	Al/M = 3.8, 7.12 atm	0.17 g/(L·min) (90)		47
CrCl2(NO)2(Ph3PO)2-(C2H5)AlCl2	chlorobenzene, 500 psig, 1 h	7.6 g/(L·min) (50)		99
CrCl2(4-Etpy)2-(C2H5)AlCl2	chlorobenzene, 500 psig, 1 h	7.5 g/(L·min) (50)		99
CrCl2(NO)2(4-Etpy)2-(C2H5)AlCl2	chlorobenzene, 500 psig 1 h	7.9 g/(L·min) (50)		99
CrCl3(py)3-(C2H5)AlCl2	chlorobenzene, 750 psig 1 h, Al/Cr = 5	6.8 g/(L·min) (50)		99
CrCl3(Bu3P)2-(C2H5)AlCl2	chlorobenzene, 500 psig, 1 h, Al/Cr = 5	7.5 g/(L·min) (50)		99
RhCl3·3H2O	EtOH-HCl, 4 atm	3.2×10^{-4} g/min (33)	E_a = 13.6 kcal/mol	33
[RhCl(C2H4)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
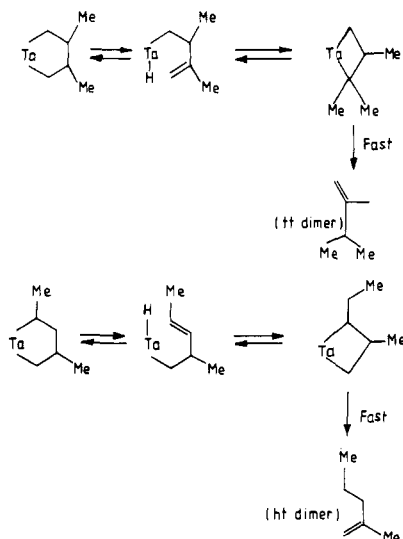
lective catalytic dimerization of propylene to a mixture of tail to tail (tt) and head to tail (ht) dimers[94] (eq 17).

$$(17)$$
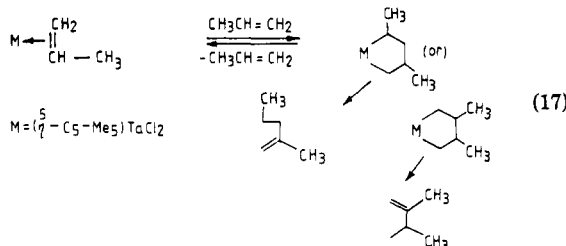
The investigators of the above work have also observed that $(\eta^5\text{-}C_5H_5)Cl_2TaCH_2CHMeCHMeCH_2$ is the crucial intermediate in the catalytic dimerization of propylene to largely 2,3-dimethyl-1-butene. Unfortunately this catalyst system becomes inactive after ~20 turnovers, possibly because $Ta(\eta^5\text{-}C_5H_5)Cl_2(C_3H_6)$ 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).

$$(18)$$
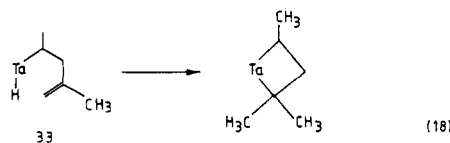
This is much more sterically crowded than the α,β-disubstituted metallacycle given in the original pathway. This choice is applicable only to α,β'-disubstituted metallacyclopentane rings since the β,β-disubstituted metallacyclopentane must collapse to the much more crowded α,α,β-trimethyltantalacyclopentane 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–$PhNH_2$–$Et_3Al_2Cl_3$ 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–$OHC_6H_4COOCH_3$[381] system gives 94% conversion and 99% selectivity to hexenes. On the other hand, the WCl_6–$C_6H_5CH_2OH$ 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 $FeCl_3$–$AlCl_3$ (1:1) system with $AlPr_3$ cocatalyst is a good catalyst for propylene dimerization. It has higher activity than the $MnCl_2$–$AlCl_3$–$AlPr_3$ system.[384] The $Fe(acac)_2$–$(i\text{-Bu})_2AlCl$ 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 $CoCl_2$–Et_2AlCl with methylene chloride has high activity for propylene dimerization. The following types of catalyst

SCHEME XXIV. H(N₂)CoL₃ (Where L = Tertiary Phosphine) Catalyzed Dimerization of Propylene
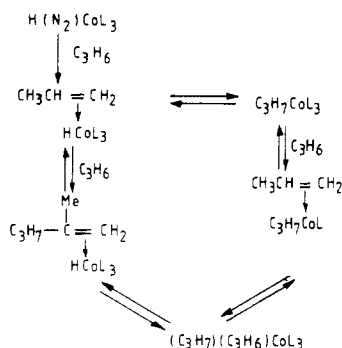
systems have also been used:[387] CoX₂–AlR₃; CoX₂–AlX₃ and related systems; CoX₂–AlX₃–AlR₃ (R = alkyl; X = halogen). Many of these systems have very high activities. The transition-metal salts give >95% selectivity to dimerization in some cases. The dimer products are similar in all cases and consist 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 CoCl₂–AlCl₃ (1:1) complex system with AlPr₃ is effective for homogeneous dimerization of propylene. It has higher activity compared to the MnCl₂–AlCl₃–AlPr₃ and FeCl₃–AlCl₃–AlPr₃ systems.[384]

HCo(N₂)(PPh₃)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(N₂)(PPh₃)₃[388] or Co(N₂)(PPh₃)₃[389] as catalysts under mild conditions can be described by eq 19, where

$$Rate = \frac{k_3 K_1 K_2 [Co][C_3H_6]}{[PPh_3] + K_1 + K_1 K_2 [C_3H_6]} \qquad (19)$$

K_3, K_1, and K_2 are all constants. The following activation parameters are reported for the dimerization reaction: ΔE_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-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 NH₃–H₂O 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 AlCl₃,[1,30,107,149,246] TiCl₄, MoCl₅, VOCl₄, and WCl₃[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 PPh₃ to P(i-Pr)₃ the yield of n-hexenes decreases gradually from 21.6 to 1.8% according to the order PPh₃ > Ph₂P(CH₂)₃PPh₂ > Ph₂PCH₂Ph > Ph₂P(i-Pr) > Ph₂PCH₂PPh₂ > PMe₃ > PEt₃ > P(n-Bu)₃ > P(CH₂Ph)₃ > P(NEt₂)₃ > Cy₂PPCy₂ > PCY₃ > P(i-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
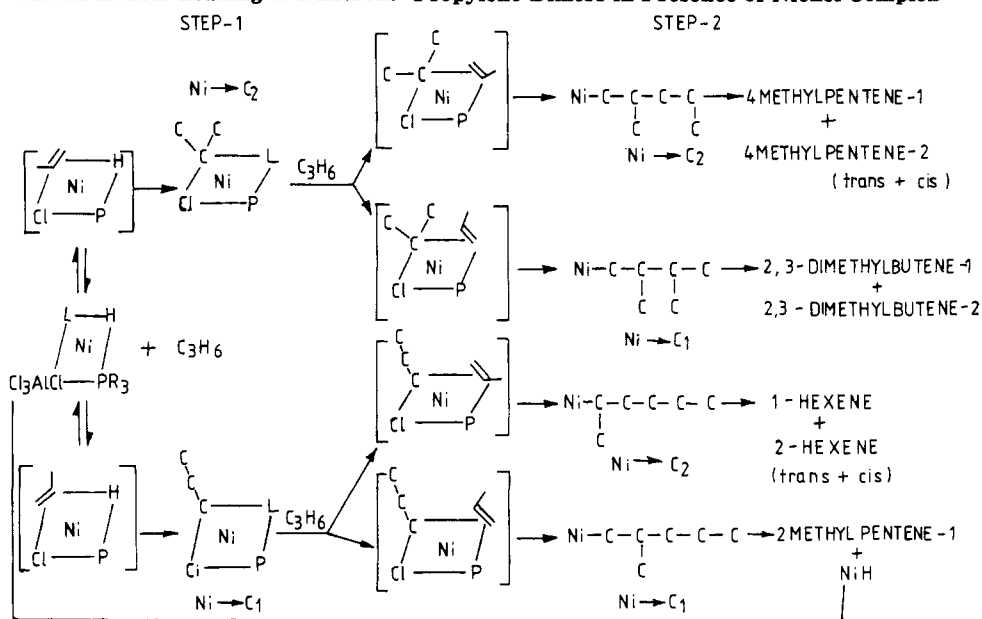
in the first reaction step (%) in the scheme is given by the ratio

$$\frac{Ni \rightarrow C_2}{Ni \rightarrow C_1} = \% \text{ (4-methyl-1-pentene} +$$

4-methyl-2-pentene + 2,3-dimethyl-1-butene + 2,3-dimethyl-2-butene)/{% (hexenes + 2-methyl-1-pentene)}

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

$$\frac{Ni \rightarrow C_2}{Ni \rightarrow C_1} = \% \text{ (4-methyl-1-pentene} +$$

4-methyl-2-pentene + hexenes)/ {% (2,3-dimethyl-1-butene + 2,3-dimethyl-2-butene + 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 $[\pi\text{-crotyl})NiCl]_2\text{-}TiCl_4$ 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 $\sim13\%$ 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.

$Ni(acac)_2\text{-}Et_2Al(OEt)$[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.

$Ni(acac)_2(i\text{-Bu})_2$ AlCl 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$_2$O$_3$, SiO$_2$, or K$_2$CO$_3$. The catalytic activity of Ni-(acac)$_2$ with Et$_2$AlCl, Et$_3$Al$_2$Cl$_3$, 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-Bu)$_2$AlCl 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$_2$O$_3$ or SiO$_2$ in combination with the (i-Bu)$_2$AlCl 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$_3$Al$_2$Cl$_3$–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-Bu)$_2$AlCl–L (L = PPh$_3$, PCy$_3$, or (Me$_3$C)$_2$PBr) has been studied.[412] The isomerizing activity of phosphorous ligands is PPh$_3$ > catalyst without L > PCy$_3$ > (Me$_3$C)$_2$PBr. 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$_3$C)$_2$PBr 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$_3$Al$_2$Cl$_3$–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$_3$Al$_2$Cl$_3$ 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 × 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$_3$·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$_3$·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$_4$H$_8$) supported on polystyrene containing PEt$_2$, P(i-Bu)$_2$, P(OEt)$_2$, P(NEt$_2$)$_2$, and PCl$_2$. AlCl$_3$ along with Et$_2$AlCl, EtAlCl$_2$, or (i-Bu)$_2$AlCl 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$_2$R$_{6-x}$Cl$_x$ (x = 2, 3, or 4) brings about the dimerization of propylene.[107,145,146] Ni(O$_2$C C$_{15}$H$_{31}$)$_2$–Bu$_2$AlCl–L (L = dibenzo-18-crown-6, polyethylene glycol 2000, X(CH$_2$CH$_2$O)$_2$CH$_2$CH$_2$X 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$_2$CR)$_2$ (R is undefined)–(i-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$_3$·OEt$_2$,[422,423] and Ni(PPh$_3$)$_4$–Et$_2$AlCl or –Et$_3$Al$_2$Cl$_3$[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·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·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-$(i$-$PPr_3)(C_2H_4)_2$ and $Ni(i$-$PPr_3)_2(C_2H_4)$ with BF_3·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] $Ni(i$-$PPr_3)(C_3H_6)_2$ 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).

$$(20)$$
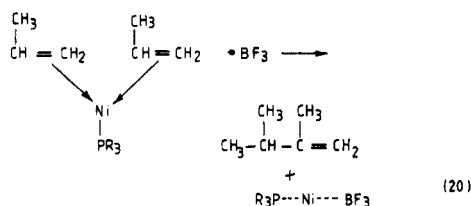
This observation leads to the conclusion that propylene ligands in the starting complex are coordinated rigidly in a "methyl to methyl" orientation and are not capable of free rotation relative to the coordination axis at −78 °C. The final adducts are active catalysts of olefin dimerizations.

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·OEt_2 also the same carbonyl complex can convert propylene into dimers.[423] The activity of various cocatalysts decreases in the order $NbF_5 > SbF_5 > TaF_5 > BF_3$·$OEt_2 > AlCl_3 > InBr_3$. 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·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-$Bu)_2AlCl$ increases in the order of solvents $C_6H_5CH_3 < m$-$Br_2C_6H_4 < C_6H_5Br < o$-$Cl_2C_6H_4$. Halogenated hydrocarbons participate in the regeneration of the catalytic complexes and also allow secondary cationic oligomerization of propylene.

The 1:2 $HNiCl$ and $P(i$-$Pr)_3$ 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).

$$(21)$$
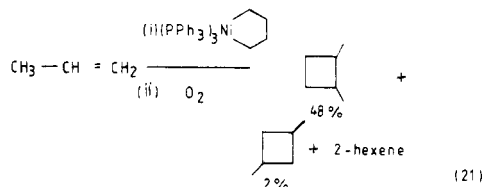
A selective dimerization of propylene to 2,3-dimethylbutene[436] catalyzed by $R_4P[(i$-$Pr_3P)NiCl_3]$ with $Et_3Al_2Cl_3$ in a toluene medium is reported. 2- and 4-methyl-1-pentene are the other products. The increasing temperature (−20 to +20 °C) leads to the formation of C_9 olefins at the expense 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

35

P = Triisopropylphosphine

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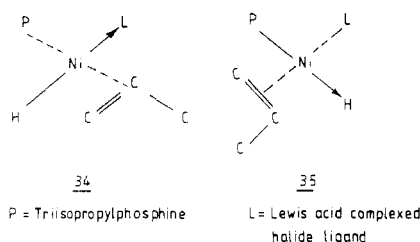
The nickel–butadiene complex deposited on PCl_3-treated Al_2O_3 and activated with $AlEt_3$[437] shows good catalytic activity for the dimerization of propylene giving predominantly 2-methyl-2-pentene in halogenated hydrocarbons and 4-methyl-2-pentene in pentane. The Ni/Al ratio of 1:200 is optimum for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

SCHEME XXVI. The "Transoid" (a) and "Cisoid" b) Orientations of the Nickel-Bis(propylene) -Aluminum Chloride Complex
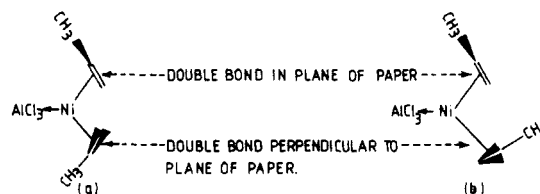
SCHEME XXVII. Dimerization Mechanism for the "Transoid" Orientation
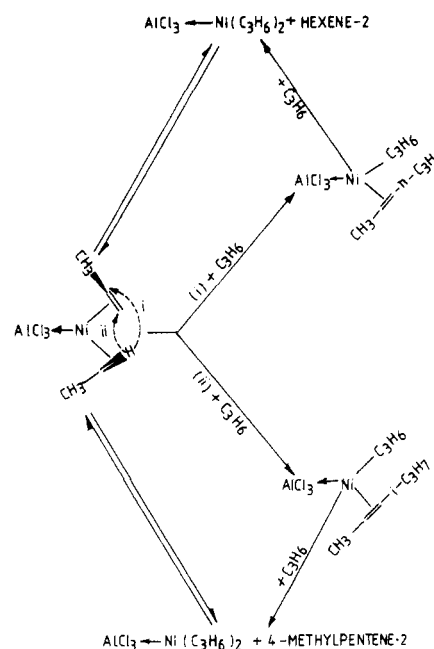
ment can take place via metal d orbitals of suitable symmetry. The mechanism for the two orientations are shown in Schemes XXVII and XXVIII.

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

$RhCl_3\cdot3H_2O$ 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
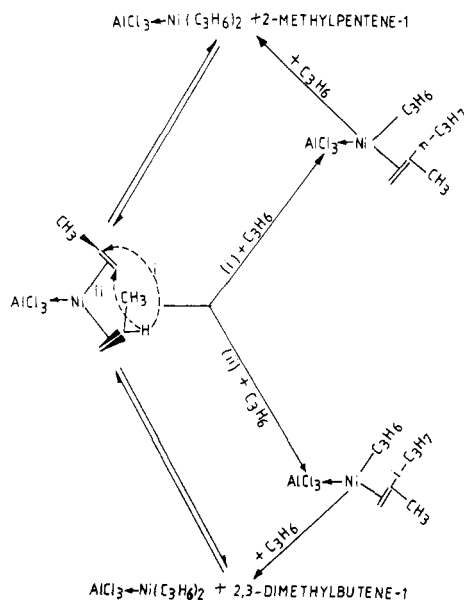
high proportions (65–90%) of straight chain hexenes are formed. However, in the presence of a cocatalyst like EtAlCl$_2$ and additives (PPh$_3$, AsPh$_3$, or SbPh$_3$) 2-methylpentene is the predominant product.[438] Pd-(olefin)Cl$_2$[171] catalyzes the reaction to give 100% n-hexene selectively. When 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 ≥ 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 ≤ Al/Pd ≤ 25 with an optimum around 20. **36** is the proposed structure for the active species where P is the phosphine.
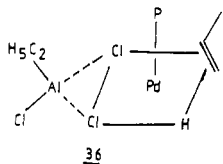
I. Rare-Earth Elements

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$_3$Al$_2$Cl$_3$, 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$_3$Al$_2$Cl$_3$ 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	E_a = 11.7 kcal/mol	360-364
organoaluminum compounds			E_a = 14 kcal/mol	370
organoaluminum compounds				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
$(C_2H_5)_3Al_2Cl_3-P(O\text{-dodecyl})_3$	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		
$(TiOR)_4-(C_2H_5)_3Al$	chloroalkanes, 0-50 °C, 1-10 atm	unspecified dimers	$AlR_3/Ti(OR)_4$ < 10	46
$Ti(OR)_4-(C_2H_5)_3Al$		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/cm², 5 h	4-methyl-1-pentene (43%), 4-methyl-2-pentene (1.8%), n-hexene (9%), 2-hexenes (46.4%)		374
$CH_3TiCl_3-(CH_3)AlCl_2$ $(\eta\text{-}C_4H_6)_2Ti(dmpe)$	CH_2Cl_2/toluene, -70 °C	2,3-dimethyl-1-butene		78, 375 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	2-methyl-2-pentene		105
$Fe(acac)_n-(C_2H_5)_2AlCl\text{-COD}$ (n = 2 or 3) $Fe(acac)_2-(Me_2CHCH_2)_2AlCl/(C_2H_5)_2AlCl/(C_2H_5)AlBr_2$	heptane/toluene	2-methyl-2-pentene, 4-methyl-1-pentene, 4-methyl-2-pentenes, 2-methyl-2-pentenes, n-hexenes (major), 2-methyl-1-pentene, 2,3-dimethylbutenes (minor)		386 385

Catalyst	Conditions	Products	Notes	Ref
$FeCl_3$-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%), 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)	109, 388, 394, 465
$(Co(PBu_3)_2Cl_2$-$R_{6-x}Al_2Cl_x$		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 L=Ph_2PN⬠Ph_2PN	methylpentenes, 25 °C, 3 bar, 6 h	2-methyl-1-pentene (85%)		469
$Co(acac)_2$-$(C_2H_5)AlBr_2$/$(i\text{-}C_4H_9)AlCl$/$(C_2H_5)_2AlCl$/$(C_2H_5)_3Al_2Cl_3$/$(C_2H_5)AlCl_2$		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–AlBr₃–PPh₃/PCy₃	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 η³-allylic nickel complexes–(C₂H₅)AlCl₂	chlorobenzene, 25 °C	2,3-dimethylbutenes (2%), methylpentenes (67%), hexenes (31%)	Al/Ni molar ratio = 15.5; conversn of propylene is 95%	404, 405
Al₂O₃–SiO₂ supported Ni(π-allyl)₂/ Al₂O₃–SiO₂–WO₃ supported Ni(π-allyl)₂–CH₃AlCl₂		hexenes, methylpentenes		406
NiL₂–(i-C₄H₉)₂AlCl–PR₃/P(OR)₃ (L = AcAcH⁻, Cl⁻, I⁻, NO₃⁻; R = alkyl, isoalkyl, Ph)	toluene/octane, 1 atm	hexenes		401, 413
Ni[Hf(acac)]₂–(i-C₄H₉)₃Al	toluene, 80 °C	hexenes (77.8%), 4-methylpentenes (4.3%), 2-methylpentenes (17.2%), 2,3-dimethylbutenes (0.8%)		474
Ni(acac)₂–(C₂H₅)₃Al/(C₂H₅)₂(OC₂H₅)Al/ (C₂H₅)(OC₂H₅)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-1-pentene (10.7%), 2-methyl-2-pentene (5.6%)	selectivity to linear olefins is 78%	385, 407, 475, 476
Ni(acac)₂–(C₂H₅)₃Al₂Cl₃–PPh₃	–50 to 40 °C	2-methylpentenes, 2,3-dimethylbutenes	Ni/Al/P mole ratio = 1:45:16	411
Ni(acac)₂–(i-C₄H₉)₂AlCl–PPh₃/Pcy₃/ (Me₃C)₂PBr		4-methyl-1-pentene (23%), other dimers		412
Ni(acac)₂–(C₂H₅)₃Al₂Cl₃–R₃P (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(C₄H₉)₃ > PBu₃	142, 401
Ni(acac)₂–(C₂H₅)₃Al₂Cl₃–PPh₃	toluene, 30 °C	n-hexenes, and methylpentenes	cat./cocat./PPh₃ = 1:8:3; order with respect to propylene = 2, order with respect to cat. = 2	393, 414
Ni(acac)₂–(C₂H₅)₃AlCl₃–PPh₃	toluene, –50 to –22 °C	n-hexenes, methylpentenes, 2,3-dimethylbutenes	propylene/nickel mol ratio = 240–2400; rate = k [Ni][C₆H₆], Eₐ = 13 kcal/mol	415
Ni(acac)₂–(C₂H₅)₃Al–PPh₃–BF₃·OEt₂	toluene/benzene/ chlorobenzene	methylpentenes, hexenes, 2,3-dimethylbutenes	Ni(acac)₂/Al(C₂H₅)₃/(PPh₃)/ BF₃·OEt₂ = 2:1:4:35	416
Ni(acac)₂(COD)/Ni(acac)₂(C₄H₆)– polystyrene-containing PEt₂/ P(i-Bu)₂/P(OEt)₂/P(NEt₂)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–(C₄H₉)₃Al	250 °C, 1800 psi	2-methylpentenes		477
Ni(acac)₂–(C₂H₅)₂ClAl–H₂O	5 kg/cm², 0° –50 °C, 5 min	dimer, higher oligomers	dimer/oligomer = 93%	478, 479
Ni(acac)₂–(C₂H₅)₃Al–PhC≡CH	xylene	2-methyl-1-pentene (53%), 2-methyl-2-pentene (41%)		480
Ni(acac)₂–R₆₋ₓAlClₓ (x = 2–4)–PPh₃	CH₂Cl₂, 600 psig, 40 °C, 17 h	n-hexenes (31%), 2-methylpentenes, 2,3-dimethylbutenes	linear hexenes is 31%	252, 481–484
Ni(acac)₂–(C₂H₅)₃Al₂Cl₃–PPh₃	30 °C, 1.5–3.2 atm, nitrogen, 3 h	C₆ alkenes (major), C₉ olefins (minor)	propylene conversn to dimers is 92%	485
Ni(acac)₂–R₃Al–BuPCl₄		methylpentenes, 2,3-dimethylbutenes, hexenes, higher oligomers		486

catalyst	conditions	products	notes	ref
Ni(acac)₂-(C₂H₅)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-(C₂H₅)AlCl₂-PCy₃	chlorobenzene, 9 atm, 27 °C, 2-3 min	C₆ olefins, C₉ olefins		488, 489
Ni(acac)₂-(C₂H₅)₂AlCl/(C₂H₅)AlCl₂-1,5-COD	toluene/CHCl₃, 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-R₆₋ₓAl₂Xₓ-BrP(CMe₃)₂	aromatic hydrocarbon/haloaromatic hydrocarbons/CCl₄, -20 to +30 °C	4-methyl-1-pentene	P/Al/Ni ratio = 1-12:10-150:1	490
Ni(acac)₂-(C₂H₅)₃Al₂Cl₃-PPh₃	1.58 atm, 30 °C, 31.5 h	C₆ olefins	Ni(acac)₂/PPh₃/(C₂H₅)₃Al₂Cl₃ mole ratio = 1:8:32	491
Ni(acac)₂-(C₂H₅)₃Al₂Cl₃-PCy₃	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-(C₂H₅)₂AlCl-P₂O₅		methylpentenes, dimethylbutenes, hexenes	P/Ni/Al = 5:1:10	493
Ni(acac)₂-(C₂H₅)₂Al(OC₂H₅)-PPh₃		2-hexene, 1-hexene, 2,3-dimethylbutenes		496
Ni(acac)₂-xH₂O-(C₂H₅)₂Al(OC₂H₅)	toluene, 40 °C, 680 psig, 17.25 h	hexenes (80%)	linearity 76%	494, 495
Ni(acac)₂-(C₂H₅)₂Al(OC₂H₅)-(C₂H₅)₄Sn/(C₄H₉)₄Sn	heptane, 40 °C, 600 psig	unspecified dimers		476
Ni(L₂)-(C₂H₅)₂Al(OC₂H₅) (L = CF₃COCH₂COCF₃)	toluene, 58-60 °C, 1.6 h	n-hexene (72-80%), nonenes (20%), dodecenes (0.2%)	propylene conversn is 80%	267
Ni(acac)₂-(C₂H₅)₂AlCl/(C₂H₅)AlCl₂-PBu₃	hexane/chlorobenzene, 59-63 °F	methylpentenes (69%), n-hexenes (11%), 2,3-dimethylbutenes (20%)	cat. efficiency is 38000 g/g of Ni, selectivity to C₆ olefin is 85%	497
Ni(PhCOCHCOPh)₂-(C₂H₅)₂Al(OC₂H₅)	ethylene glycol-dimethyl ether-toluene, 40 °C, 17 h	linear hexenes (77%)		498
polymer gel immobilized Ni(acac)₂-(C₂H₅)AlCl₂/(C₂H₅)₂AlCl	n-heptane/2,2,4-trimethylpentane	hexenes	activity decreases in the order NiCl₂ > NiBr₂ > Ni(NO₃)₂ > NiSO₄	276, 409
Ni(acac)₂ and an inorganic Ni salt supported on Al₂O₃/SiO₂-[(CH₃)₂CHCH₂]₂AlCl		C₆ olefins		410, 499
Ni(acac)₂ on alkaline earth metal carbonate or oxide-R₆₋ₓAl₂Clₓ	organic solvents	hexenes	major products are C₆ olefins (2,4-dimethyl-1-butene)	500
Ni(acac)₂ supported on Al₂O₃ or aluminosilicate-(C₄H₅)₃Al₂Cl₃-(i-Pr₃)P		C₆ olefins (67-85.0%), C₉ olefins (13.0-27.8%), higher oligomers (2-6.4%)		501
Ni(acac)₂ supported on SiO₂-Al₂O₃-R₆₋ₓAl₂Xₓ-PR₃	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(O₂CR)₂-(C₂H₅)₂AlCl (RCO₂H = octenoic acid, oleic acid)		hexenes, nonenes, and dodecenes (minor)		419, 504
Ni oleate-i-Bu₂AlCl	tert-butyltoluene, <20 °C, 1.5 Kg/cm²	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(O₂CR)₂-(C₂H₅)AlCl₂-CF₃CO₂H (RCO₂H = C₉-C₁₃ carboxylic acids)	isooctane, 15 bar, 42 °C, 3 days	hexenes, nonenes	91% conversn of propylene in the presence of CF₃CO₂H and 70% conversn in the absence of the additive	506

TABLE IV (Continued)

cat. system	reactn conditns	products	comments	ref
Ni(OAc)₂-(C₂H₅)₂AlCl₂-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%), C₉ olefins		270
Ni(O₂CR)₂-R₆₋ₓAl₂Xₓ-PPh₃/PX′₃ (X′ = halogen, alkoxy group)	0 to 10 °C, 1 atm	C₆ olefins	≤90% selectivity to methylpentenes	324, 325, 418
Ni(O₂CR)₂-(C₂H₅)₂AlF (HO₂CR = 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(O₂CH)₂-(C₂H₅)₂AlCl₂	40 °C, 3 h	2-methyl-2-pentenes		478
Ni(O₂CR)₂-(C₂H₅)₃Al₂Cl₃/(C₂H₅)AlCl₂ (RCO₂H = isopropylsalicylic acid, C₁₇ 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(O₂CR)₂-(C₂H₅)₂Al₂Cl₃ (RCO₂H = 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(O₂CR)₂-(C₂H₅)₆₋ₓAlXₓ-PPh₃/PCl₃/P(i-Pr)₃ (CO₂H = 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(O₂CR)₂-AlCl₃-(C₂H₅)₃Al (RCO₂H = octenoic acid)	toluene, 10 °C	2-methyl-2-pentene (major)	yield of dimers is 96.1%	513
Ni(O₂CR)₂-PCl₃-(C₂H₅)₃Al (RCO₂H = octenoic acid)	toluene, 1 h, 0 °C	2-methyl-1-pentene (6%), 2-methyl-2-pentene (55%), 4-methyl-1-pentene (0.4%), 4-1methyl-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-(C₂H₅)₃Al-BF₃·Et₂O	toluene, 50 °C, 1 h	dimer (92%)		515
Ni(CH₃COCH₂CO₂)₂-(C₂H₅)₂AlCl-C₂H₅AlCl₂	2-methyl-1-pentene/4-methyl-2-pentene, 25 °C, 1 h	2-methyl-2-pentene		227
Ni(O₂CR)₂-(C₂H₅)₃Al-SnCl₄ (RCO₂H = octenoic acid)	toluene, 10 °C		yield of dimers is 87.7%	516
Ni(O₂CR)₂-(C₂H₅)₃Al/[(C₂H₅)₂Al]₂O-PCY₃/isoprene (RCO₂H = naphthenoic acid)	toluene, 20 °C, 4 kg/cm², 3 h	mixture of dimers	conversn to dimers is 79.4%, selectivity to α-olefins is 58.7%	238, 517, 518
Ni(Bu)(CS₂O)-(C₂H₅)₂AlCl-H₂O	5 kg/cm², 0-50 °C, 5 min	2-methyl-2-pentene, 4-methylpentenes, other dimers and oligomers	dimer/oligomer = 93%	478, 479
NiCl₂(PPh₃)₂-R₆₋ₓAl₂Xₓ (x = 2, 3, or 4)	toluene, 20 °C	n-hexene, 2-methylpentenes, 2,3-dimethylbutenes, 4-methyl-2-pentenes (85%), C₉ olefins (15%)		280, 619
NiCl₂[PPh(cyclohexyl)₂]-(C₂H₅)₂AlCl-H₂O	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
NiX₂(PR₃)₂-R₆₋ₓAl₂Xₓ (X = Cl, Br; R = Bu, Ph; x = 2, 3, or 4)	chlorobenzene	C₆ olefins	cocat./cat. = 2	253, 281, 510, 521
NiCl₂(PPh₃)₂/NiCl₂(PPh₂H)₂/	0-25 °C	C₆ olefins		466, 522

catalyst system	conditions	products	comments	ref
$NiCl_2(dppe)/NiCl_2(PCy_3)_2/NiBr_2(PCy_3)_2/NiCl_2(P\text{-}i\text{-}Pr_3)_2\text{-}(C_2H_5)_3Al_2Cl_3/(C_2H_5)_2AlCl/C_2H_5)AlCl_2$	61.8 °C, 25 kg/cm²	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
$NiCl_2(PBu_3)_2\text{-}(C_2H_5)_2AlCl/(C_2H_5)AlCl_2\text{-}(CH_3)_3CCl$				525
$NiCl_2(PPh_3)_2\text{-}(C_2H_5)AlCl_2\text{-}(PPh_3)_2Mo(NO)_2Cl_2$	50 psi, 25 °C	C₆ olefins (30.3%) and higher olefins		526
$NiCl_2(Ph_2PCH{=}CHPPh_2)\text{-}(C_2H_5)AlCl_2$	chlorobenzene, 16–20 °C, 30 psig, 1.5 h	C₆ olefins	Al/Ni ratio = 5:20	527
$NiSO_4(PPh_3)_2\text{-}CH_3AlCl_2/(C_2H_5)AlCl_2$	−10 to 10 °C; chlorobenzene, 0 °C, 860 mm	2-methyl-2-pentenes; 2,3-dimethylbutenes	Al/Ni ratio of 20:1 is used; rate = 250 kg of product/h/g of Ni	501, 528
$NiCl_2(i\text{-}PPr_3)_2\text{-}(C_2H_5)_3Al_2Cl_3\text{-}C_7H_{16}N$	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
$NiCl_2(PPh_3)_2\text{-}(C_2H_5)AlCl_2$	heptane/chlorobenzene, 0 °C, 100 mm	C₆ olefins (90%), C₉ olefins (10%)	Al/Ni = 2:1 for (C₂H₅)₃Al; Al/Ni = 4:1 for (C₂H₅)₃Al₂Cl₃	530
$NiCl_2(i\text{-}PPr_3)_2\text{-}(C_2H_5)_3Al/(C_2H_5)_3Al_2Cl_3$		n-hexenes, 2-methylpentenes, 2,3-dimethylbutenes		297
$NiX(PPh_3)_3\text{-}AlCl_3$				531
$NiCl_2(PPh)_3\text{-}AlCl_3\text{-}(C_2H_5)_3N\text{-}Ph_3P/Bu_3P$	PhCl, 20 °C	4-methyl-1-pentene, 4-methyl-2-pentene, 2-methyl-2-pentene (major product), 2,3-dimethylbutene		422, 423, 532
$NiCl(PPh_3)_2/NiCl(PPh_3)_3\text{-}BF_3\text{-}OEt_2\text{-}$ Brønsted acids	halogenated hydrocarbons	hexenes, methylpentenes		434
$NiCl_2(PR_3)_2\text{-}(i\text{-}C_4H_9)_2AlCl$ (R = cyclohexyl)		2,3-dimethylbutenes	isomerization increases in the order when R = PhMe < m-Br₃C₆H₄ < PhBr < o-Cl₂C₆H₄	124
$HNiCl(i\text{-}PPr_3)_2\text{-}(C_2H_5)_3Al_2Cl_3$		C₆ olefins		286
$NiCl_2(PBu_3)_2$ deposited on $SiO_2\text{-}Al_2O_3\text{-}(C_2H_5)_2AlCl$		hexenes, 2,3-dimethylbutenes, 2-methylpentenes		533
$NiClCPh_3\text{-}AlBr_3\text{-}PPh_3$	chlorobenzene	dimer and trimer (small amounts)		297
$Ni(PR_3)_2(ethylene)\text{-}AlCl_3$		n-hexene, 2-methylpentenes, 2,3-dimethylbutenes		534
$Ni(PEt_3)_2(CF_2{=}CF)Cl\text{-}(C_2H_5)AlCl_2$	9.2 °C, 30 psig, 30 min	C₆ olefins		535, 536
$Ni(COD)_2\text{-}(C_2H_5)_3P/2\text{-}Cl\text{-}1,3\text{-}butadiene/p\text{-}ClC_6H_4COCl$		C₆ olefins		150, 300, 301, 435
$NiCl_2L_2\text{-}R_{6-x}Al_2Cl_x\text{-}PR_3$ (L = tetramethylcyclobutadiene)	chlorobenzene/benzene	n-hexenes, 2-methylpentenes, 2,3-dimethylbutenes		537, 538
$Ni(CH_2{=}CHCN)_2\text{-}R_{6-x}Al_2Cl_x\text{-}PR_3$	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		426, 427, 433
$Ni(ethylene)[(P(OC_6H_4R)_3]_2$ (R = Me, OMe)$/Ni(ethylene)(PPh_3)_2\text{-}(C_2H_5)_3Al\text{-}CF_3CO_2H/H_2SO_4/PPh_3$		C₆ olefins	highest activity for Et₃Al₂Cl₃	123
$Ni(ethylene)_2[P(i\text{-}C_3H_7)_3]\text{-}TiCl_4/WCl_6$	−78 °C	trans C₆ olefins		429
$Ni(propylene)_2(P\text{-}i\text{-}Pr_3)\text{-}BF_3$		2,3-dimethyl-1-butene (90%)		437
$Ni(C_2H_4)_2$ deposited on PCl_3 treated $Al_2O_3\text{-}(C_2H_5)_3Al$	halogenated hydrocarbon/pentane	2-methyl-2-pentene, 4-methyl-2-pentenes	Ni/Al ratio = 1:200	122
$Ni[P(i\text{-}Pr)_3]_2(C_2H_4)/NiP(i\text{-}Pr)_3(C_2H_4)\text{-}BF_3{\cdot}E_2O/AlBr_3/HCl$		2,3-dimethylbutenes (36.6%), 2-methylpentenes (59.9%), hexenes (3.5%)		

TABLE IV (Continued)

cat. system	reactn conditns	products	comments	ref
Ni[P(OPh)3]4–AlCl3/AlBr3/(C2H5)3Al2Cl3	toluene, chlorobenzene, CH2Cl2	n-hexene, isohexene	optimum activity at Al/Ni ratio of 5:1 to 7:1; n-hexene/isohexene ratio = 3:7	433
Ni(PPh3)3(CH2)4–O2	toluene	2-hexene, 1,2-dimethylcyclobutane		155
R4P[(i-Pr)3PNiCl3]–(C2H5)3Al2Cl3		2,3-dimethylbutene, 2-methyl-1-pentene, 4-methyl-1-pentene		436
R(bpy)]NiX [R = Ph, o-, m-, p-MeC6H4, o-Cl-C6H4, X = I, Cl, Br]–EtAlCl2/Et2AlCl	–16 °C	2-methyl-2-pentene, 4-methyl-2-pentene	Al/Ni = 100	438
Ni(CO)4–AlCl3–PPh3		2-hexene, 4-methyl-2-pentene, 2,3-dimethyl-1-butene	max activity with 2:1 phosphine/AlCl3	440
NiCl2 and NiCl2 treated on a solid carrier–(C3H7)3Al/(C2H5)3Al2Cl3/(Me2CHCH2)3Al2Cl3		2-methyl-2-pentene, 4-methyl-2-pentene, 2-hexene		384
NiX2 (X = halide) –alR3	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–RAlX2	–20 to 50 °C, 1–5 atm	2,3-dimethyl-2-butene		539
nickel salt–RAlX2	hydrocarbons, 20–60 °C,	C6 olefins		540
Ni(acac)2–(C4H9)3Al–BCl3	1800 lb/in.2	2-methyl-1-pentene		541
Ni(acac)2 on SiO2–Al2O3–(C2H5)3Al2Cl3–PPh3/PBu3	145 °F, 3 h	2,3-dimethylbutene (10.9%), 2-methylpentene (66.95%), n-hexene (23.13%), nonene, decene		263
Ni oleate–Al2R6-xClx		n-hexene, 2-methylpentene		458
Ni naphthenate–(C2H5)3Al–PPh3–2,4,6-Cl3C6H2OH		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(PR3)2–NbF5/MoF6/SbF5/TaF5/AsF5/WF6/PF5/VF5 (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(PPh3)2 supported on acidic, calcined Al2O3–SiO2	toluene, 140–160 °F, 70 min	2,3-dimethylbutenes (15%), 2-methylpentenes (53%), hexene (16%), C9 olefins (15%)		295, 544
Ni(PPh3)4–BF3–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(PPh3)4 attached to polystyrene–BF3–OEt2–H2O	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)(PPh3)–(C2H5)AlCl2	chlorobenzene, 28 psi, 35 °C, 3.5 h	n-hexene, 2-methylpentenes, 2,3-dimethylbutenes	44% wt of cocat. is mixed with catalyst	547
(R4P)2(NiCl4)–(C2H5)3Al2Cl3	chlorobenzene, N2, 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
(R4P)(NiBr3PR3)–R6-xAl2Clx	chlorobenzene, 0 °C, 15 min,	n-hexene, 2-methylpentenes,	Al/Ni ratio is 30:1	549

catalyst	conditions	products	remarks	ref
NiX₂–AlCl₃–PR₃	100 mm propylene	2,3-dimethylbutenes n-hexene, 2-methylpentenes, 2,3-dimethylbutenes		269, 316, 550
NiBr₂–(i-C₄H₉)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
NiCl₂–Et₃Al₂Cl₃–(i-C₃H₇)₃P	o-dichlorobenzene, 1 h, –10 °C	2,3-dimethylbutenes	conversn of propylene = 90–5%; selectivity to the product 76–81%	551
NiCl₂/NiBr₂–(C₂H₅)₂AlCl–PPh₃/PBu₃		2,3-dimethylbutenes	the product yield increases with increase in basicity of ligands	552
NiCl₂–(C₂H₅)₃Al–HCl/(i-C₃H₇)₃P/ butadiene	chlorobenzene, 35–40 °C, 15 atm, 9 h	C₆ olefins and C₉ olefins		553
NiCl₂/NiCl₂ supported on a solid carrier–(C₃H₇)₃Al/(C₂H₅)₃Al₂Cl₃/ (i-C₄H₉)₂AlCl–AlCl₃		2-hexenes, 2-methyl-2-pentenes, 4-methyl-2-pentenes	activity of the heterogenized cat. are comparable with that of homogeneous cat.	384, 554
NiBr₂L₂–(C₂H₅)₃Al₂Cl₃ (L = hexamethylphosphoramide)		n-hexenes (68%), 41-methylpentenes (28%)		315, 555
NiCl₂L₂ (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–(C₂H₅)₃Al/(C₂H₅)₂Al(OEt)		n-hexene (75–80%), 2-methylpentenes (20–25%)		475, 476
NiCl₂(BuNH₂)₄–(C₂H₅)AlCl₂ NiSO₄(BuNH₂)₄/NiSO₄(py)₄/ Ni(ClO₄)₂(py)₄/NiSO₄(RNH₂)₂/ (CH₃)AlCl₂/(C₂H₅)AlCl₂ (RNH₂ = lutidine)	chlorobenzene –10 to 10 °C, <1 kg/cm²	2-methyl-2-pentene (60%) 2-methyl-2-pentene		557 527
Ni(NO₃)₂(py)₄–(C₂H₅)AlCl₂	chlorobenzene, 0 °C, 20 min	2-methyl-2-pentene (51%)		514
NiL₂–(C₂H₅)AlCl₂ (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)PPh₃Cl–(C₂H₅)₂AlCl	toluene, –15 ± 2 °C, 70 min	dimethylbutene (10%), methylpentene (74%), hexene (16%)		559
Ni[poly(4-vinylpyridine)]–(C₂H₅)AlCl₂/ (C₄H₉)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(Me₂SO)₆][NiCl₄]–(C₂H₅)₃Al₂Cl₃	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(R₂SO)₆][MX₄]–(C₂H₅)₃Al₂Cl₃ (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 C₆ containing up to 75% methylpentenes; addition of moisture increases reaction rate	562
NiCl₂(Ph₂SO)–(C₂H₅)₃Al₂Cl₃	1-chloronaphthalene, 2.5 min, 0 °C	methylpentenes (75.2%), n-hexene (22.4%), 2,3-dimethylbutenes (2.4%)		563
NiL₂–(C₂H₅)₂AlCl/(C₂H₅)AlCl₂–KOH (L = salicylaldimine)	chlorobenzene, 30 min, 20 °C	hexene, nonene		564
NiL₂ supported on bochmite– (C₂H₅)₃Al₂Cl₃/(C₂H₅)₂AlCl (L = n-butylsalicylaldimine)	chlorobenzene, 20 °C	C₆ olefins (72%), C₉ olefin (20%), higher oligomers		326

TABLE IV (Continued)

cat. system	reactn conditns	products	comments	ref
CuAlCl4/Cu2Cl2-(C2H5)2AlCl	isooctane, 1 atm	**Copper** 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
ZnAl2Cl6-(C2H5)AlCl2/(C2H5)2AlCl		**Zinc** trans-4-methyl-2-pentene		33
(η-C4H9)2Zr(dmpe)		**Zirconium** 2,3-dimethyl-1-butene		81
(π-allyl)ZrBr3/(benzyl)ZrBr3-(C2H5)2AlCl/(C2H5)AlCl2		C6 olefins, higher α-olefins		332
Zr(acac)4-(C2H5)3Al2Cl3-PPh3/PBu3	155 °F	C6 olefin		376
RR'nR2NbAlm [R = cyclopentadienyl, Me-substituted cyclopentadienyl, Me3C-CH2; R' = PhCH3, Me3C-CH2; n = 0, 1; R2 = Me3CCH, PhCH, (CH2)4, CH2(CHMe)2CH2; A = halogen; m = 1, 2]-YR3R4R5 [Y = N, P, As, Sb, Bi; R3, R4, R5 = alkyl, aralkyl, PhCMe2CH2CH2, aryl]	decane	**Niobium** C6 olefin		377
RhCl3-HCl	CHCl3/PhNO2	**Rhodium** C6 olefins (major), 2-methyl-2-pentene		160
RhCl3·3H2O		n-hexene (43%), 2-methylpentene (57%)		171, 337
RhCl3·3H2O-BiPh3/SbPh3		n-hexene (15%), 2-methylpentene (85%)		565
RhCl3·3H2O	alcohol	mixed dimers		161
Rh2Cl2(SnCl3)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
PdCl2/PdCl2(BZCN)	CHCl3/CH2Cl2/anisole	**Palladium** hexenes (65-90%)	with PdCl2(BZCN) isomerization of olefin takes place	171, 173, 337
PdCl2-(C2H5)AlCl2-PPh3/AsPh3/SbPh3		2-methylpentenes (predominant)		565
PdCl2	acetic acid, HCl	mixed hexenes		336
Pd(acac)2-(C2H5)AlCl2-PR3 (R = Bu, OPh)	CH2Cl2	n-hexenes (95%)	replacement of PR3 by P(OR)3 increases the rate but lower selectivity	345, 441
[(π-allyl)PdCl]2-(C2H5)AlCl2-P(OR)3		unspecified dimers		239
PdL2-(C2H5)AlCl2	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
AgAlCl4-(C2H5)AlCl2/(C2H5)2AlCl		**Silver** trans-4-methyl-2-pentene, 2-methyl-2-pentene		33

catalyst	conditions	products	remarks	ref
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				
$WCl_6\text{-}(C_2H_5)_3Al_2Cl_3\text{-}MeNH_2/c\text{-}C_6H_{11}NH_2/PhNH_2/p\text{-}XC_6H_4NH_2$ (X = Cl, Br, CH₃, 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 conversn of propylene is 39%; selectivity for C₆ olefins is 98%	379, 380
$WCl_6/WBr_5\text{-}(C_2H_5)AlCl_2\text{-}2,4,6\text{-}R_3C_6H_2NH_2$ (R = H, Br, Cl)	chlorobenzene, 60 °C, 1 h	C₆ olefins		207
$WCl_6\text{-phenols-}(C_2H_5)_3Al_2Cl_3\text{-}PhNH_2$		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
$WCl_6\text{-}BzOH\text{-}(C_2H_5)_3Al_2Cl_3\text{-}PhNH_2$		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
$WCl_6\text{-}(RCO)_2CH_2\text{-}(C_2H_5)_3Al_2Cl_3\text{-}PhNH_2$ (R = Me, CMe₃, Ph)	chlorobenzene	4-methylpentene (5.3-6.3%), 2,3-dimethyl-1-butene (43-54%), 2-methyl-1-pentene (28-31%)	WCl₆/(RCO)₂NH₂ mole ratio = 1:1; conversn of propylene is 69-74% with selectivity to dimers 76-92%	383
Platinum				
$PtCl_2\text{-}(C_2H_5)AlCl_2$		n-hexene (40%), 2-methylpentene (60%)		565
Cerium				
$Ce(acac)_3\text{-}(C_2H_5)_3Al_2Cl_3\text{-}PPh_3$	chlorobenzene, 600 psig, 95 °F, 3.5 h	2-methylpentenes and 2,3-dimethylbutenes (78%), n-hexenes (22%)	conversion of propylene is 8%	442
$Ce(acac)_3\text{-}(C_2H_5)_3Al_2Cl_3\text{-}PPh_3$	chlorobenzene, 100-125 °C, 150 psig, 60 min	C₆ olefins	yield of dimer is lower in the absence of PPh₃	443
Thorium				
$Th(NO_3)_4\text{-}(C_2H_5)_3Al_2Cl_3\text{-}PPh_3$	chlorobenzene, 350-500 psig, 115-120 °C, 2.5 h	C₆ olefins	yield of dimers is 61%	444
$Th(NO_3)_4\text{-}(C_2H_5)_3Al_2Cl_3\text{-}PPh_3$	chlorobenzene, 115-120 °F, 150-1500 psig, 3 h	2,3-dimethyl-1-butene, 2-methyl-2-pentene	cat./PPh₃ 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, [Ph₃P]/[cat.] = 1	2.22 g/(L·min) (25)	data for various [Ph₃P]/[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·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 scarce. 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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