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CATALYTIC SYNTHESIS OF 1,4-HEXADIENE BY A NICKEL-BASED CATALYST. FACTORS CONTROLLING ACTIVITY AND SELECTIVITY

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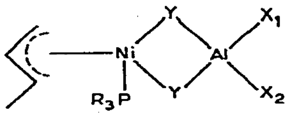
SUMMARY

The nature of the phosphine ligand and the aluminum cocatalyst strongly affect activity and stereoselectivity in the Al/Ni/P type (*e.g.* $R_nAlX_{3-n}+NiX_2\cdot 2\,PR_3$ or $Ni^0[L]+R_3P$) catalyst system to synthesize *trans*- and *cis*-1,4-hexadiene from ethylene and butadiene.

Catalyst activity is highest when the P to Ni ratio is 1. Catalyst selectivity shifts toward the *trans* isomers and catalyst activity decreases as the electron acceptor ability of the phosphine is increased.

Catalyst activity goes from zero to a maximum as the chlorine content of the cocatalyst R_nAlCl_{3-n} is increased with no influence on stereoselectivity. The selectivity in forming *trans*-1,4-hexadiene increases significantly when the cocatalyst consists of a 1/1.5 to 1/2.0 mixture of $RAlCl_2$ and R_2AlB ($B = OR$, or NR_2; R_2AlB alone is not a cocatalyst). By use of selected phosphine ligands and aluminum cocatalysts, almost all *trans*-1,4-hexadiene can be synthesized.

The increase in catalyst selectivity is attributed to the steric and stereoelectronic effects which the ligand and the cocatalyst impose on the nickel atom. These cause the butadiene to interact in the *s-trans* configuration which leads to the formation of *trans*-1,4-hexadiene. Comparison of the reaction properties of various types of catalyst combinations suggests an active catalyst species whose structure is of the type



where Y is generally a halogen and X is an alkyl, a halogen, or other non-inhibiting group.

INTRODUCTION

The catalytic synthesis of 1,4-dienes from 1,3-dienes and ethylene employing a variety of transition metal catalysts has been studied by a number of workers[1-9].

The use of a multicomponent nickel-based catalyst system, $(Bu_3P)_2NiCl_2 + i\text{-}Bu_2AlCl$, for the codimerization of ethylene and butadiene to form predominantly *trans*- and *cis*-1,4-hexadiene has been reported by Miller, Kealy, and Barney[7]. Recently, Tolman[9] also reported the slow formation of 1,4-hexadiene by heating ethylene and butadiene in the presence of $[(RO)_3P]_4Ni^+HPF_6^-$. The above works shed some light on the nature of the intermediates in the catalytic reactions and help to explain the various by-products formed during the process. However, little has been said about the role played by phosphorus ligands and the cocatalyst in determining the course of the reaction. We have extended the work to relate the nature of each of the catalyst components with the reaction properties of the catalyst system. Special emphasis has been placed on controlling the stereospecific synthesis to produce *trans*-1,4-hexadiene, an intermediate in the synthesis of some EPDM elastomers.

RESULTS AND DISCUSSION

The catalyst system

The catalyst system used earlier by Miller[7] was not convenient in terms of varying the catalyst components independently. In the present work we have used a three-component catalyst system represented in general as follows:

$$Ni^0Cod_2 + R_3P + R_xAlCl_{3-x} (Ni/P/Al = 1/1/3\text{–}6)$$

where Ni^0Cod_2 is the hydrocarbon soluble cyclooctadienenickel(0) complex[10].

This catalyst is long-lived and, like the Miller catalyst, formed primarily 1,4-hexadiene, 3-methyl-1,4-pentadiene, and 2,4-hexadiene from ethylene and butadiene. A typical product distribution formed by this catalyst and by the $(Bu_3P)_2NiCl_2/i\text{-}Bu_2AlCl$ catalyst is shown in Table 1.

TABLE 1

CATALYTIC SYNTHESIS OF 1,4-HEXADIENE[a,b]

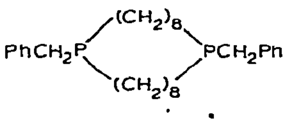
Catalyst	BD[b] Conv. (%)	1,4-HD[b] (%)	*T/C*[b]	3-MeP[b] (%)	2,4-HD[b,c] (%)	Higher boiling olefins (%)
$i\text{-}BuAlCl_2 + Ni^0\ Cod_2 + Bu_3P$[a]	77	69	2	8.1	8.2	~15
$i\text{-}BuAlCl_2 + Ni^0\ Cod_2 + Ph_3P$[b]	66	66	4	5.7	10.4	~17
$i\text{-}Bu_2AlCl + (Bu_3P)_2NiCl_2$[d]	33	65	~2.5	8	3–4	~22

[a] Catalyst ratio Ni/Al/P = 1/5/1; reaction time 60 min. [b] See experimental for details of reaction conditions and calculations. BD = butadiene; 1,4-HD = 1,4-hexadiene; *T/C* = ratio of *trans*-1,4-/*cis*-1,4-hexadiene; 3-MeP = 3-methyl-1,4-pentadiene; 2,4-HD = 2,4-hexadiene. [c] The yield of 2,4-hexadiene increases with increasing conversion. [d] Ref. 7.

The phosphine ligand

With the catalyst system described above, we have found that only one phosphine ligand is required for maximum activity. In the presence of more than one phosphine per nickel, the catalyst will remain active only if the amount of the aluminum cocatalyst exceeds that of the phosphine. Bidentate phosphines, such as Ph_2PCH_2–

CH_2-PPh_2, reduced the catalyst activity as much as several hundred-fold even in the presence of excess aluminum cocatalyst*. Bidentate ligands having long methylene chains, *e.g.*:



do not inhibit the catalytic reaction. The above results indicate that the active species in the catalyst system involves a 1/1 complex of nickel and a phosphine.

The 1,4-hexadiene produced by the Miller[7] catalyst contained both the *trans* and the *cis* isomer at a ratio of 2.5/1 to 2.8/1. During the early part of our work with the present catalyst system, we consistently noticed an increase in the *trans/cis* ratio (T/C) when triphenyl phosphine Ph_3P was used instead of tributylphosphine Bu_3P (Table 1). Since Ph_3P is a better electron acceptor ligand than Bu_3P as well as being larger, the change of the *trans/cis* ratio could be due to an electronic as well as a steric effect.

The electron donor–acceptor properties of trisubstituted phosphine ligands can be evaluated by comparing their ability to change the C–O stretching frequency in a phosphine transition metal carbonyl complex, *e.g.* $(R_3P)_xM(CO)_y$[14–17]. Meriwhether[18] and more recently Tolman[19] have used this technique to arrange various substituted phosphines according to their "electron donor–acceptor" strengths.

We have tested a number of trisubstituted phosphines of varying acceptor strength and steric requirements as ligands in our catalyst system. We found an

TABLE 2

THE INFLUENCE OF PHOSPHINE LIGANDS ON THE CODIMERIZATION REACTION WITH $NiCod_2$ AND $i\text{-}BuAlCl_2$

R_3P	$\nu(CO)$ (A_1)	T/C[a]	3-MeP[a] (%)	Rel. react. rate[b]	1,4-HD (%)[b]
$(C_6H_{11})_3P$	2056.4	1.5	17.0	2.0	83
Bu_3P	2060.3	2.0	14.0	1.25	82
$Allyl_2PhP$	2065.3[d]	2.9	8.0		
Ph_3P	2068.9	4.0	8.0	1.0	80
$(m\text{-}CF_3C_6H_4)_3P$	2074.1[e]	5.0	7.5		
$(C_6F_5)Ph_2P$	2074.8	6.0	6.0	0.7	60

[a] The isomer distributions were measured at <25% butadiene conversion. T/C = *trans/cis* ratio of 1,4-hexadiene; 3-MeP = 3-methyl-1,4-pentadiene. [b] Relative rates were measured by the time required to achieve 43% conversion of butadiene under the same reaction conditions. Yield of 1,4-hexadiene at 43% conversion of butadiene. [c] Ref. 19. [d] Value for Me_2PhP from ref. 19. [e] Value for $(m\text{-}FC_6H_4)_3P$ from ref. 19.

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* These ligand effects are analogous to those reported in the nickel-catalyzed dimerization of propene. Wilke[12] observed that a catalysts system containing Ni/P/Al = 1/1/2 could be completely inhibited by addition of one additional equivalent of phosphine. Hata[13] has reported that $Ni(CO)_2(Ph_3P)_2/AlCl_3$ is an active dimerization catalyst whereas $Ni(CO)_2(Ph_2PCH_2CH_2PPh_2)/AlBr_3$ is inactive.

It is interesting to note that bidentate ligands of the type $Ph_2PCH_2CH_2PPh_2$ have been found to be ideal for the synthesis of *cis*-1,4-hexadiene using an Fe- or Co-based catalyst[3–5].

increase in the T/C ratio with increasing acceptor property of the phosphines. The T/C ratio increased from 1.5/1 to 6/1 as the ligand changed from the weakest acceptor, $(C_6H_{11})_3P$, to the strongest acceptor, $Ph_2(C_6F_5)P$ (Table 2). With even stronger acceptor ligands such as $Ph(C_6F_5)_2P$ or $(C_6F_5)_3P$, the catalyst lost its property as a hexadiene catalyst and became instead primarily a catalyst for oligomerization of butadiene. This might be due to incomplete bonding of these bulky phosphines at the concentrations used. The catalyst thus behaves as if no phosphine were present.

We were not able to draw any conclusion as to whether the size of the phosphine ligand alone has any direct effect on the *trans* to *cis* ratio since the donor acceptor property of the trisubstituted phosphine also changes with changing the size of the substituents[19]. However by comparing the relative effect of the three phosphines, $(C_6H_{11})_3P$, Ph_3P (Note: these two phosphines are of comparable size) and Bu_3P, we expect its influence, if any, to be much less significant than the electronic effect.

Interestingly, an increase in T/C ratio is accompanied by a decrease in the quantity of the by-product 3-methyl-1,4-pentadiene and by a general decrease in the reaction rate (Table 2).

The aluminum cocatalyst

The Al cocatalyst contributes very significantly to the reaction property of the catalyst system. In the catalyst system reported by Miller[7] the $(Bu_3P)_2NiCl_2$ can be reduced by the dialkylaluminum chloride, generating the corresponding monoalkylaluminum dichloride and a lower valent nickel most likely an Ni^0 compound:

$$2\,R_2AlCl + L_xNiCl_2 \rightarrow Ni^0(L)_y + 2\,RAlCl_2 + RR$$

The effective cocatalyst could be either the dialkylaluminum chloride originally charged or the alkylaluminum dihalide formed during the reduction.

To clarify the role of the aluminum component in the actual codimerization reaction the following catalyst combinations have been tested:

(a) $Ni^0Cod_2 + Ph_3P + i\text{-}Bu_2AlCl$

(b) $Ni^0Cod_2 + Ph_3P + i\text{-}BuAlCl_2$

(c) $Ni^0Cod_2 + Ph_3P + i\text{-}Bu_2AlCl + i\text{-}BuAlCl_2$

(d) $Ni^0Cod_2 + Ph_3P + i\text{-}Bu_3Al$

Catalyst (d) was inactive; catalyst (a) had low activity, while catalysts (b) and (c) were very active. The much greater activity of $i\text{-}BuAlCl_2$ as a cocatalyst over $i\text{-}Bu_2AlCl$ is shown in Fig. 1. The activity of the $i\text{-}Bu_2AlCl$ catalyst could be increased to close to that observed with $i\text{-}BuAlCl_2$ by addition of 20 mole % $i\text{-}BuAlCl_2$*.

Monoalkyl- and dialkylaluminum chloride differ not only in Lewis acidity but in their alkylation ability. In the above experiment, since alkylation on Ni^0Cod_2 is unlikely, the difference in activity between $RAlCl_2$ and R_2AlCl can be attributed to the difference in their Lewis acidity. This was confirmed by testing $AlBr_3$ and $AlCl_3$ as cocatalysts. The combination $NiCod_2/Ph_3P/AlBr_3$ did indeed prove to be a very

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* The relatively high activity achieved by Miller[7] with $(Bu_3P)_2NiCl_2/i\text{-}Bu_2AlCl$ catalyst is probably related to formation of monoalkylaluminum dihalide *in situ*.

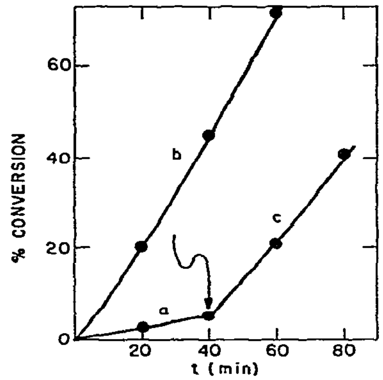


Fig. 1. Comparison of cocatalyst activity of i-Bu_2AlCl and i-$BuAlCl_2$ with $NiCod_2$ and Ph_3P. a = Ni^0Cod_2 + Ph_3P + 5 i-Bu_2AlCl; b = Ni^0Cod_2 + Ph_3P + 5 i-$BuAlCl_2$; c = addition of 2 i-$BuAlCl_2$ to (a) after 40 min of reaction.

active codimerization catalyst; but the reaction was complicated by considerable polymerization of butadiene and by a much more extensive isomerization of 1,4- to 2,4-hexadiene; both of these may be caused by excess free $AlBr_3$. By using an Ni^{II} complex with a more basic phosphine, $(Bu_3P)_2NiCl_2$, and limiting the level of $AlCl_3$ or $AlBr_3$ to 2–3 equivalents, it was possible to prepare 1,4-hexadiene with reasonable yield at low conversions. The *activity* of this system in forming C_6 dienes exceeded the corresponding i-$BuAlCl_2$ catalyst system (Table 3) but the *selectivity* in forming 1,4-hexadiene was considerably lower.

TABLE 3

RATE OF BUTADIENE CONVERSION BY $(Bu_3P)_2NiCl_2$ WITH VARIOUS COCATALYSTS

R_nAlX_{3-n} (Al/Ni = 6)	Time (min) for 25% conversion of butadiene
i-Bu_2AlCl[a]	60
i-$BuAlCl_2$[a]	~15
$AlCl_3$[b]	~10

[a] Al/Ni ratio 6. [b] See experimental; the Al/Ni ratio is not meaningful in this case as the $AlCl_3$ is only slightly soluble in toluene.

The Lewis acidity of the aluminum cocatalyst can also be reduced by forming a complex with electron donors such as ethers. We found that in the presence of a slight excess of diethyl ether the activity of the catalyst $RAlCl_2 + Ni^0Cod_2$ was greatly reduced while no significant change in activity occurred in the presence of a corresponding amount of the more weakly basic diphenyl ether. Table 4 lists the relative catalyst activity of various types of Al cocatalyst.

Most of the aluminum cocatalysts described so far did not affect the *T/C* ratio of the hexadiene formed even though they greatly affect the rate of reaction. It was, therefore, surprising to find that *trans* to *cis* ratio increased (regardless of the types of phosphine used) when the cocatalysts were derived from a suitable combination of alkylaluminum halides and an alkylaluminum alkoxide or amide, R_nAlB_{3-n} ($B = OR$ or NR_2). As can be seen from Table 4, the above combination also caused a substantial drop in the catalyst activity. This effect can be expected with a lower overall Lewis acidity of the mixed cocatalyst. The effect of these cocatalysts on the *T/C* ratio of the product is very dependent upon the ratios of the two aluminum components. The combination which formed the highest proportion of *trans*-hexadiene had a ratio $R_2AlB/RAlCl_2 = 1.5$ to 2 (Table 5).

TABLE 4

RELATIVE RATE OF HEXADIENE SYNTHESIS USING VARIOUS ALUMINUM COCATALYSTS WITH $Ni^0Cod_2 + Ph_3P$

Aluminum cocatalyst[a]	Relative rate[b]
$i\text{-}Bu_3Al$	0, inactive
R_2AlOR	0, inactive
$i\text{-}Bu_2AlCl$	<1
$i\text{-}BuAlCl_2$	10
$AlBr_3$[c]	Fast but complicated
$i\text{-}BuAlCl_2 \cdot [PhOPh]_x$[d]	7–9
$i\text{-}BuAlCl_2 \cdot [Et_2O]_y$[e]	<1
$EtAlCl_2$	>10
$EtAlCl_2 + Et_2AlB$ ($B = OR$, NR_2)	1–5

[a] No change in *T/C* ratio can be observed when the same R_3P was used except in the case of Et_2AlB.
[b] Rate measured at butadiene conversion less than 25%. [c] Produce both C_6 dienes and polymeric butadiene even at low conversion of butadiene. [d] $x = 1$–5. [e] $y = 1$–2.

TABLE 5

EFFECT OF THE RATIO OF $R_nAlCl_{3-n}/R_mAlB_{3-m}$ ON THE *trans/cis* RATIO OF 1,4-HEXADIENE[a,b]

Phosphine	Aluminum cocatalyst	*trans/cis* ratio
Ph_3P	$EtAlCl_2$	4–4.5
Ph_3P	$EtAlCl_2 + Et_2AlOEt$	4–4.5
Ph_3P	$EtAlCl_2 + 2\ Et_2AlOEt$	6–7
Ph_3P	$EtAlCl_2 + 3\ Et_2AlOEt$	6–7[b]
Ph_3P	$EtAlCl_2 + 2\ i\text{-}Bu_2AlNEt_2$	6
$C_6F_5PPh_2$	$EtAlCl_2$	6
$C_6F_5PPh_2$	$EtAlCl_2 + Et_2AlOEt$	6
$C_6F_5PPh_2$	$EtAlCl_2 + 1.5\ Et_2AlOEt$	15–19
$C_6F_5PPh_2$	$EtAlCl_2 + 2\ Et_2AlOEt$	10–12
$C_6F_5PPh_2$	$2\ i\text{-}Bu_2AlCl + EtAl(O\text{-}i\text{-}Pr)_2$	10
$C_6F_5PPh_2$	$EtAlCl_2 + 2\ i\text{-}Bu_2AlNEt_2$	10

[a] Catalyst $Ni(Cod)_2$. [b] Reaction rate decreases rapidly with increasing $Et_2AlOR/EtAlCl_2$ ratio.

This narrow range for the effective ratio led to a more detailed examination of the above cocatalyst mixture. Alkylaluminums are known to exist in varying types as well as degrees of association[20]. It seemed possible that of the complexes possible from R_xAlCl_{3-x} and R_nAlB_{3-n}, only one type is effective for increasing the *trans* to *cis* ratio. Evidence for the formation of such a complex was obtained from an analysis of the NMR spectra of mixtures of $EtAlCl_2$ and Et_2AlOEt shown in Fig. 2. Et_2AlOEt is known to exist exclusively in the dimeric form[21], its NMR spectrum shows four peaks corresponding to the absorption of protons on $AlCH_2CH_3$ and $AlOCH_2CH_3$ (Fig. 2b). The NMR spectrum of $EtAlCl_2$, which also exists primarily in dimeric form through chloride bridges[20,22], is shown in Fig. 2a. In mixtures of Et_2AlOEt and $EtAlCl_2$ at a ratio of less than 1/1 (Fig. 2c) there is no discernible shift in the ^1H resonance indicating no significant breaking up of the original associated structures.

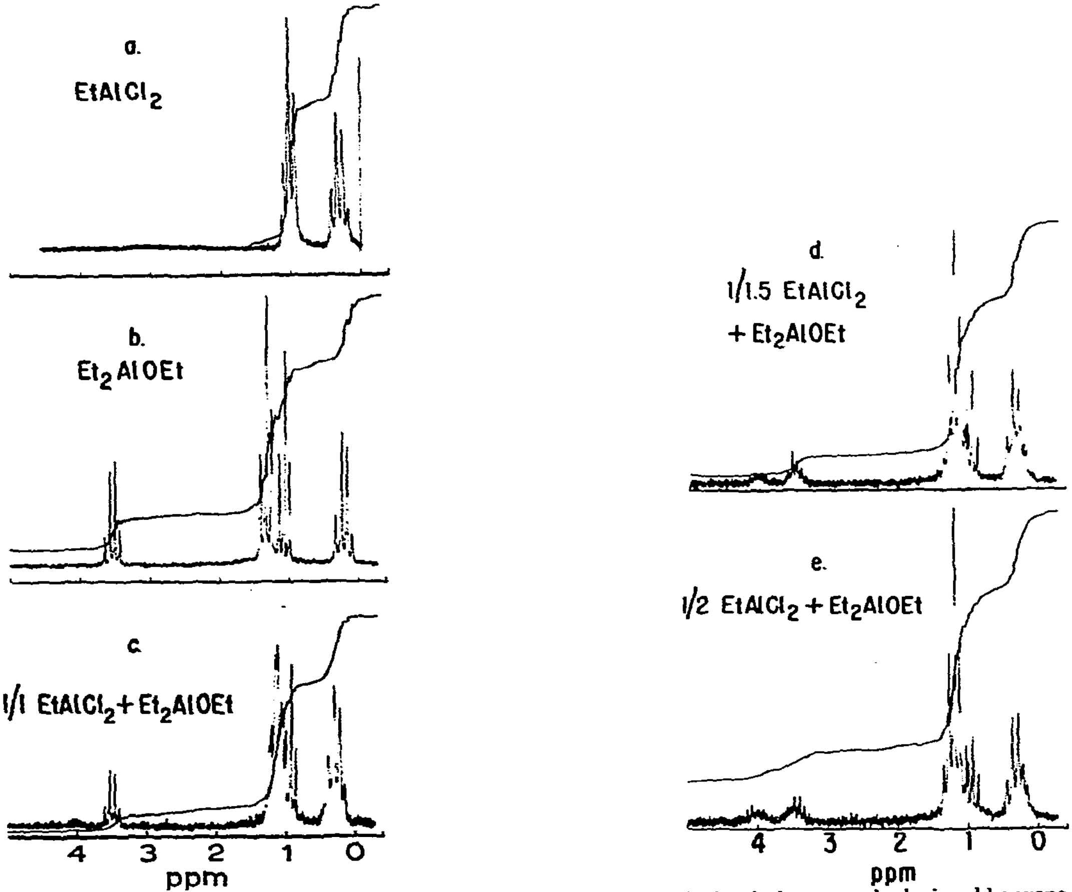
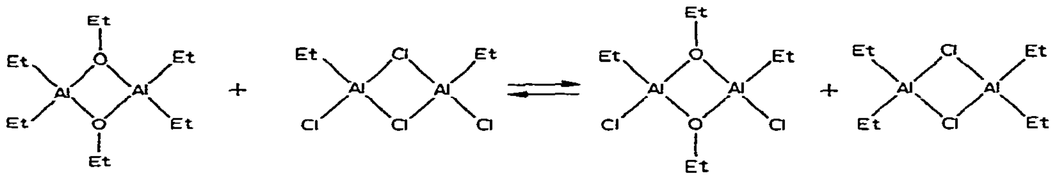


Fig. 2. NMR spectra of mixtures of Et_2AlCl and Et_2AlOEt. 10% solution in benzene; lock signal benzene at 7.37 ppm.

At the ratio of 1.5/1 a distinct new peak can be seen at 4 ppm (Fig. 2d). This new peak gets somewhat bigger when the ratio is increased to 2/1 (Fig. 2e). We attribute the 4 ppm peak to a new methylene proton absorption as a result of changes imposed on some of the OEt groups. This downfield shift indicates that the oxygen atom in OEt has become more electron deficient[23] than in the original dimeric complex of Et_2Al-OEt suggesting ligand exchange to form a new species with both the Cl and OEt groups bonded to the same Al atom. A very probable reaction might involve a Cl^- and Et^- exchange to form complex (I) and Et_2AlCl:

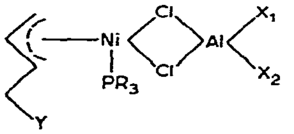


(I)

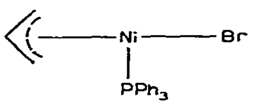
A small shift in the methyl and methylene absorptions of the $CH_3CH_2Al<$ region from the 1.0 and 0.25 ppm of $EtAlCl_2$ toward the 1.33 and 0.45 ppm characteristic of Et_2AlCl[24] is consistent with formation of some Et_2AlCl in the reaction mixture. A complex such as (I) might be responsible for increasing the *T/C* ratio.

Mechanistic implications

A. Basic catalyst species and catalytic reactions. Previous work by Miller[7] suggested the presence of a π-crotyl–nickel intermediate during the catalytic process. We found that only one phosphine ligand per nickel was required for maximum catalytic activity. Since an alkylaluminum halide is also needed as cocatalyst, the active form of the catalyst species can be represented as a complex of structure (II):



(II)



(III)

(II) ($X_1 = X_2 =$ alkyl, halide; $Y = H$)
(IIa) (X_1, X_2, $Y =$ halide)
(IIb) ($X_1 = X_2 = Cl$, $Y = C_4H_8AlClR$)

A good model for the Ni moiety of structure (II) is the π-allylnickel bromide triphenylphosphine complex (III). The latter alone does not catalyze hexadiene synthesis, but upon addition of alkylaluminum halides or aluminum trihalide* (III) is transformed into a very active catalyst.

A comparison of the catalytic activity of (III) with that of $(Ph_3P)_2NiCl_2$ and $NiCod_2 \cdot Ph_3P$ using $i\text{-}Bu_2AlCl$ as a cocatalyst is shown in Fig. 3. The lack of a noticeable induction period and the high level of activity for the combination (III)/$i\text{-}Bu_2AlCl$ is especially noteworthy. If the more acidic $RAlCl_2$ is a cocatalyst, the activities of these catalysts are much more similar to each other** (see Table 6).

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* Due to the formation of an insoluble complex as well as the presence of side reactions, the catalyst system (III)+$AlBr_3$ can not be compared on an equal basis with the alkylaluminum halide system. In general, if AlX_3 is used, an alkyl- rather than aryl-phosphine is preferred (*vide infra*).

** A relatively stable solution of (III) and $i\text{-}BuAlCl_2$ can be obtained (in the absence of monomer) which is a very active catalyst. No reduction of Ni^{II} can be observed for at least one hour. If R_2AlCl is used, reduction can be observed in a few minutes and if R_3Al is added to (III), immediate reduction to metallic nickel takes place.

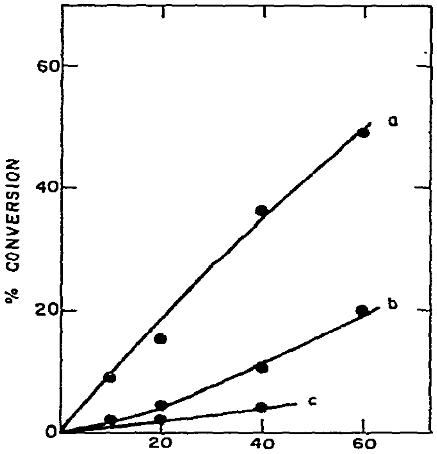


Fig. 3. Catalytic activity of various nickel phosphines with i-Bu_2AlCl as cocatalyst. a = Allyl NiBr · Ph_3P; b = $(Ph_3P)_2NiBr_2$; c = $NiCod_2 \cdot Ph_3P$; Al/Ni = 5.

TABLE 6

RELATIVE ACTIVITY OF $Ni^0Cod.Ph_3P$ AND ALLYLNiBr.Ph_3P IN FORMING C_6 DIENES WITH DIFFERENT COCATALYSTS[a,b]

Catalyst	i-Bu_2AlCl	Et_2AlCl	$EtAlCl_2$
$Ni^0Cod_2 + Ph_3P$	~1	6	60
AllylNiBr · Ph_3P	8	12	65

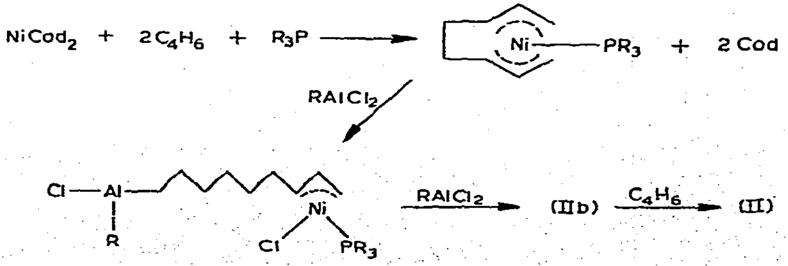
[a] Al/Ni ratio, 5/1. [b] Relative rates are based on total g of C_6 dienes formed in 20 min. The butadiene conversion was less than 25%.

The actual mechanism of formation of a species such as (II) from the starting Ni^{II} or Ni^0 compounds is speculative.

Starting from $(R_3P)_2NiCl_2 + AlX_3$ the formation of a π-allylic species could proceed as follows without invoking prereduction of Ni^{II} to Ni^0:

$$(R_3P)_2NiCl_2 + 2\,AlX_3 + C_4H_6 \rightarrow (IIa) + R_3P \cdot AlX_3$$

Analogous reactions have been postulated by Dogoplask[24] to explain the catalyst formation reaction in the catalytic polymerization of butadiene by $NiX_2 + AlX_3$.

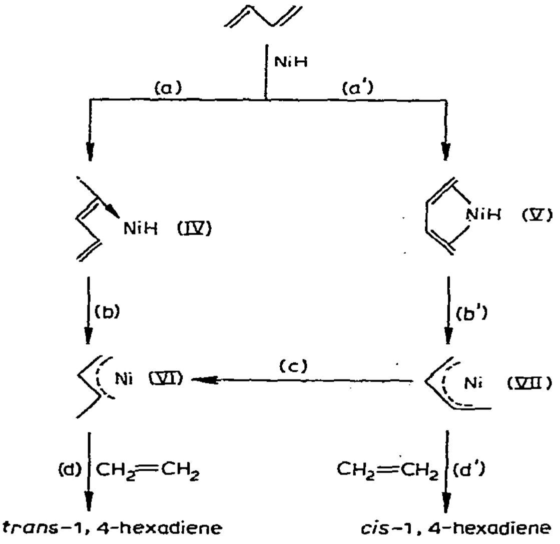


Starting with Ni^0Cod_2, the catalyst formation must involve initial conversion to a bis-π-allylic nickel complex, such as Wilke[11] has demonstrated, followed by alkyl–halogen exchange with the alkylaluminum halide.

B. Stereospecific control of cis/trans isomer distribution. Formation of 1,4-hexadiene with nickel or rhodium catalysts has been shown to involve coupling of ethylene with a π-crotyl–metal intermediate[7–9]. However, the catalytic factors which lead to the formation of the *trans* or *cis* isomers of 1,4-hexadiene have only recently been considered. Based on the work of Tolman[9] and numerous investigations on the nickel-catalyzed polymerization of butadiene the key reactions leading to these two isomers can best be represented as shown in Scheme 1.

SCHEME 1

REACTIONS CONTROLLING RATIO OF *trans*- AND *cis*-1,4-HEXADIENE



Reactions (a) and (a') represent different ways of coordination of butadiene on the nickel atom to form the transoid coordinated complex (IV) and the cisoid coordinated complex (V). Hydride addition to (IV) [reaction (b)] results in the formation of the *syn*-π-crotyl intermediate (VI) which then interacts, (d), with an ethylene to form the *trans*-1,4-hexadiene. Similarly, reactions (b') and (d') result in the synthesis of *cis*-1,4-hexadiene. Since the *syn*-crotyl species (VI) is thermodynamically more favorable than the *anti*-crotyl species (VII), isomerization of the latter to the former can also take place[9]. Thus, the *T/C* ratio of the hexadiene formed is determined by: (1) the ratio of species (IV) and (V); and (2) the extent of isomerization reaction, (c), before the addition of ethylene to the *anti*-crotyl species (VII). This reaction can affect the *trans/cis* ratio only when the insertion reaction (d') is slower than the isomerization reaction (c). In recent work on codimerization of butadiene and ethylene with $[(CH_3O)_3P]_4NiH^+PF_6^-$ as a catalyst, Tolman[9] has measured the rate of *syn–anti* isomerization of $\pi\text{-}C_4H_7Ni[P(OCH_3)_3]_3^+$ in CD_3CN. He found that the half-life for isomerization of the *syn* to *anti* isomer was ca. 0.36 hour at 30°; in CH_2Cl_2 the reaction was slower with a half-life of ca. two hours at 50°.

These rates of isomerization are far too slow to affect the stereoselectivity of the hexadiene formed with the catalysts considered here. With the present catalysts, reaction rates frequently approach 4000 molecules of hexadiene/Ni atom/hour at 25° (or ca. 1 hexadiene/Ni/sec). The rate of the insertion reaction, (d′), must be at least as fast as this and the isomerization reaction would have to be even faster to affect the *cis/trans* ratio of the product.

It is entirely possible that isomerization may proceed much faster with the present catalysts than with the model system considered by Tolman. To test this possibility, reactions were run at reduced ethylene concentrations; this should slow down the insertion reaction (d′) relative to the isomerization reaction (c). No effect on the *trans/cis* ratio of the product was observed while the rate of hexadiene formation was reduced over 200-fold*.

The *trans/cis* ratio of the product must, therefore, be determined at an earlier reaction stage and most probably by the ratio of species (IV) and (V) *i.e.* by the distribution of *trans*- or *cis*-coordinated butadiene. Steric or electronic factors which force the butadiene to coordinate as a monodentate ligand rather than a bidentate ligand will lead to a higher ratio of *trans*-hexadiene. A similar mechanism has been proposed to explain the formation of *cis*- and/or *trans*-polybutadiene with π-allylnickel halides as catalysts[26-31].

The two factors which affect the *trans/cis* ratio of 1,4-hexadiene, namely the phosphine and the alkylaluminum alkoxide, can be interpreted in terms of their effect on butadiene coordination.

The *T/C* ratio of 1,4-hexadiene increases as the electron acceptor ability of the phosphine increases. This can not be due to the "blocking" of a coordination site as the phosphorus/nickel ratio was 1 in all cases. The results are analogous to the formation of *trans*-polybutadiene from π-allylnickel iodides as compared to formation of the *cis*-polymer from π-allylnickel chlorides. Dolgoplosk[31] has reasoned that this is due to the increased tendency of the iodide (as compared to Cl) to form multiple bonds with the nickel by accepting electron density from the metal. Similarly, in the codimerization reactions, the more electron accepting phosphines reduce the number of effective bonds which can be formed between the metal and the butadiene***, favoring *trans* coordination of the diene (IV).

The *T/C* ratio of hexadiene is also increased by addition of aluminum cocatalysts containing OR or NR_2 ligands. We propose that this is due to selective blocking of a coordination site on the nickel by formation of an intermediate such as:

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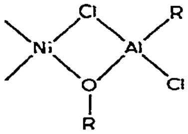
* Interestingly, on replacing the nickel catalysts with a rhodium catalyst, the *trans/cis* ratio can readily be increased by reducing the ethylene concentration[25]. This suggests that the rate of *anti–syn* isomerization relative to the rate of ethylene insertion in the crotyl–rhodium** complex might be significantly faster than that in crotyl-nickel complex.

** In the rhodium catalyst for 1,4-hexadiene synthesis, the active intermediate had been shown by Cramer[7] to be a crotyl–rhodium complex.

*** An alternative mechanism has been proposed by Natta[27] who suggested that the nickel chloride catalyst reacts monomerically in the polymerization whereas the iodide reacts as a dimer, thereby eliminating one coordination site. This mechanism can not explain the effect of phosphines on the *trans/cis* ratio of hexadiene.



In the polymerization of butadiene, Teyssie[32,33] has shown that certain electron donors such as alcohols or phosphines can convert π-allylnickel chloride from a catalyst which forms *cis*-polybutadiene to one which produces *trans*-polybutadiene. These ligands presumably block a site on the nickel atom, forcing the butadiene to coordinate by only one double bond. While alcohols can not be added directly to the hexadiene catalyst (as they deactivate the alkylaluminum cocatalysts), incorporation of the oxygen atom on the cocatalyst places it in an ideal position to coordinate with the nickel.

EXPERIMENTAL

Equipment

The reactions were carried out in a two-liter stainless steel autoclave similar to the one described in a previous publication[7]. One modification involved the installation of a sampling device which consisted of a dip tube fitted with a needle valve which can be connected either to a cold trap or a high pressure syringe* for injection into GLC.

The reaction mixture was analyzed on a Perkin–Elmer Model 800 GLC. The best column we found for the analysis consisted of a 12′ × $\frac{1}{4}$″ stainless steel tube packed with 20% G. E. "XE-60" pm Chromosorb W. At 55° and a helium flow rate of 15 cc per minute. The retention times of the C_6 components are as follows: 3-methyl-1,4-pentadiene, 5.5; *trans* 1,4-hexadiene, 7.5; *cis* 1,4-hexadiene, 8.5; *trans,trans*-2,4-hexadiene, 14; *trans,cis*-2,4-hexadiene, 15.8; *cis,cis*-2,4-hexadiene, 17 min.

The NMR spectra were recorded on a Varian association's HA100 instrument. All chemical shifts were reported as ppm downfield from tetramethylsilane.

The aluminum cocatalysts. All the aluminum derivatives except $i\text{-}Bu_2AlNEt_2$ were purchased from Texas Alkyls and were all at least 95% pure $i\text{-}Bu_2AlNEt_2$ was synthesized from $i\text{-}Bu_2AlH$ and Et_2NH using the procedure of Ziegler and Kroll[34] (% N_2 calcd. 6.6, found 6.7).

Trisubstituted phosphines. Most phosphines were purchased from Strem or Carlisle Chemical Companies (U.S.A.). (See also Acknowledgement.)

$NiCod_2$. The compound was prepared according to the procedure of Wilke[35].

General procedure for 1,4-hexadiene synthesis

All reactions are carried out under an inert atmosphere. Dry toluene (900 ml) was charged into the reactor and cooled to below −20°. About 180 g of butadiene, previously purified by passing through a column of molecular sieves, was distilled into the cooled reactor which was then allowed to warm to room temperature. Purified ethylene was then charged into the reactor to a total pressure of 80 psi at 25°.

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* Purchased from Precision Sampling Corporation, P.O. Box 15119; Baton Rouge, Louisiana 70815 (U.S.A.).

A fixed quantity of internal standard for GLC analysis (usually either cyclohexane or hexane) was injected into the reactor followed by a toluene solution containing one mmole of the nickel phosphine complex. Ethylene was fed as required to maintain a reactor pressure of 80 psi; the gas flow was monitored by a rotameter. The reactor temperature was maintained by controlled cooling using a dry ice/acetone bath. Samples were taken periodically through the sampling tube and analyzed.

The reaction was stopped by addition of isopropyl alcohol and the products were isolated in the same manner as described previously[7]. In case the catalyst was to be reused the reactor was first cooled to 0° and the reaction mixture was removed completely from the reactor through the sampling tube. It was then distilled at room temperature under reduced pressure until all the C_6 dienes and the solvent were removed, taking precautions to avoid exposure to air or moisture. The residual solution, consisting of the catalyst in high boiling olefin by-products, could be reinjected into the reactor containing freshly charged solvent and reactants.

Analytical procedure. Relative rates and comparison of isomer distributions were generally determined at butadiene conversions of less than 25 % unless otherwise noted. At this conversion the decrease in butadiene concentration does not affect the reaction rate significantly and formation of high boiling by-products is usually minimal. Measurement of the trans/cis ratio at higher conversions is less desirable due to the faster rate of isomerization of the trans relative to cis 1,4-hexadiene to the conjugated isomer. Butadiene conversion is calculated as g butadiene reacted/g butadiene charged. The yields are calculated on basis of butadiene converted.

Use of $AlCl_3/(Bu_3P)_2NiCl_2$ catalyst for codimerization reaction

When this catalyst was used, 3 mmole solid $AlCl_3$ was introduced into the reactor as a suspension in the toluene solvent. The nickel compound (1 mmole) was added after saturation of the solvent with ethylene. The data in Table 3 are for reaction in toluene for comparative purposes. Faster rates were observed in chlorinated solvents (perchloroethylene, chlorobenzene, *o*-dichlorobenzene).

Codimerization reaction at low pressure

To determine the change in *trans/cis* ratio at very low concentration of ethylene the following procedure was used:

The reactor was charged with the usual amount of butadiene and toluene. At 25° the pressure exerted by butadiene registered at 20 psi. Ethylene was allowed to flow into the reactor to create an overall pressure of 22–23 psi. A catalyst consisting of $NiCod_2/Ph_3P/EtAlCl_2$ was added. After 40 min the reaction was stopped. The reaction mixture contained less than 1 g of 1,4-hexadiene with *trans/cis* ratio of about four. It also contained several grams of polymeric butadiene as by-product.

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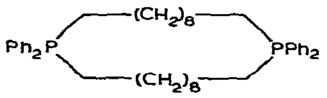

and Dr. R. Clement for sample of π-AllylNiBr · Ph_3P. The authors also wish to express thanks to Professor R. S. Nyholm; Prof. D. Bush; Drs. C. Sarafidis, F. M. Ambrecht, and C. A. Tolman for valuable discussions; and to Mr. S. Liss for his contribution to the experimental aspect of the project.

REFERENCES

1 T. ALDERSON, E. L. JENNER AND R. V. LINDSEY JR., *J. Amer. Chem. Soc.*, 87 (1965) 5638.
2 G. HATA AND D. AOKI, *J. Org. Chem.*, 32 (1967) 3754.
3 M. IWAMOTO AND S. HAGUCHI, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, 71 (1968) 237.
4 M. IWAMOTO AND S. HAGUCHI, *J. Org. Chem.*, 31 (1966) 4290.
5 M. IWAMOTO AND S. HAGUCHI, *Bull. Chem. Soc. Jap.*, 41 (1968) 150.
6 W. SCHNEIDER, *U. S. Pat.*, 3,398,209; *Chem. Eng. News*, 47 (1969) (17) 50.
7 R. G. MILLER, T. J. KEALY AND A. L. BARNEY, *J. Amer. Chem. Soc.*, 89 (1967) 3756.
8 R. CRAMER, *J. Amer. Chem. Soc.*, 89 (1967) 1963.
9 C. A. TOLMAN, *J. Amer. Chem. Soc.*, 92 (1970) 6777.
10 G. WILKE, *Angew. Chem.*, 72 (1960) 581.
11 B. BOGDANOVIC *et al.*, *Angew. Chem., Int. Ed. Engl.*, 2 (1963) 105.
12 G. WILKE *et al.*, *Angew. Chem., Int. Ed. Engl.*, 5 (1966) 163.
13 G. HATA AND A. MIYAKE, *Chem. Ind. (London)*, (1967) 921.
14 W. D. HORROCKS JR. AND R. C. TAYLOR, *Inorg. Chem.*, 2 (1963) 723.
15 F. A. COTTON, *Inorg. Chem.*, 3 (1964) 702, and references therein.
16 G. R. VAN HECKE AND W. D. HORROCKS JR., *Inorg. Chem.*, 5 (1966) 1960.
17 W. STROHMEIER AND F. J. MULLER, *Chem. Ber.*, 100 (1967) 2812.
18 L. S. MERIWETHER AND M. L. FIENE, *J. Amer. Chem. Soc.*, 81 (1959) 4200.
19 C. A. TOLMAN, *J. Amer. Chem. Soc.*, 92 (1970) 2953.
20 H. J. EMELEUS AND A. G. SHARPE, *Advan. Inorg. Chem. Radiochem.*, 7 (1965) 263.
21 R. C. GOLESWORTHY AND R. A. SHAW, *Proc. Roy. Soc., Ser. A*, 292 (1966) 1189.
22 J. BRANDT AND E. G. HOFFMANN, *Brennstoff-Chem.*, 45 (1964) 201.
23 T. TAKESHITA AND W. E. FRANKLE, *Tetrahedron Lett*, 56 (1968) 5913.
24 K. G. MUESSEROV, I. L. KIRSHEMBAUM, R. E. LOBACH AND B. I. DOLGOPLOSK, *Vysokomol. Soedin*, 10 (1968) 673.
25 A. C. L. SU AND J. W. COLLETTE, results to be published.
26 B. D. BABITSKII, B. A. DOLGOPLOSK, V. A. KORMER, M. I. LOBACH, E. I. TINYAKOVA AND V. A. YAKOLEV, *Dokl. Akad. Nauk. SSSR*, 161 (1965) 583.
27 L. PORRI, G. NATTA AND M. C. GALLAZZI, *J. Polym. Sci., Part C*, (1967) 2525.
28 E. I. TINYAKOVA, A. V. ALFEROV, T. G. GOLENKO, B. A. DOLGOPLOSK, I. A. ORESHKIN, O. K. SHARAEV, G. N. CHERNENKO AND V. A. YAKOVLEV, *J. Polym. Sci., Part C*, (1967) 2625.
29 L. PORRI, G. NATTA AND M. C. GALLAZZI, *Chim. Ind. (Milan)*, 46 (1964) 428.
30 B. D. BABITSKII, B. A. DOLGOPLOSK, V. A. KORNER, M. I. LOBACH, E. I. TINYAKOVA, N. N. CHESNOKOVA AND V. A. YAKOVLEV, *Vysokomol. Soedin*, 6 (1964) 2202.
31 B. D. DOLGOPLOSK, I. I. MOISEEV AND E. I. TINYAKOVA, *Dokl. Chem.*, 173 (1967) 340.
32 J. P. DURAND, F. DAWANS AND D. H. TEYSSIE, *J. Polym. Sci., Part A-1*, 8 (1970) 979.
33 F. DAWANS AND D. H. TEYSSIE, *C. R. Acad. Sci., Ser. C*, 261 (1965) 497.
34 K. ZIEGLER AND W. R. KROLL, *Justus Liebigs Ann. Chem.*, 629 (1960) 167.
35 B. BOGDANOIC, M. KRONER AND G. WILKE, *Justus Liebigs Ann. Chem.*, 699 (1966)