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Organometallic Catalysis in Stereospecific Polymerisation and Nature of the Active Centres

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Experimental results on the application of individual organic compounds of transition metals for the stereospecific polymerisation of dienes are summarised, and a relation is established between the nature of the metal with its surrounding ligands and the microstructure of the polymer chain. The nature of the active centres responsible for various types of stereoregulation and the mechanism of the formation of chain units are discussed. Aspects of copolymerisation in coordinated systems are considered. Research results on the mechanism of the cleavage of cycloalkenes and the dismutation of alkenes are clarified, arguments are given in favour of a chain process and a carbene character for the active centres, and the mechanism of individual stages in the process is examined. A list of 207 references is included.

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I. INTRODUCTION

The present paper summarises experimental results on organometallic catalysis in the stereospecific polymerisation of dienes and cycloalkenes. Research has been devoted mainly to elucidating the nature of the active centres exerting different stereospecific effects in the polymerisation of conjugated dienes, and to studying the mechanism of a novel type of chain reactions—the polymerisation of cycloalkenes and the dismutation of alkenes under the influence of carbene complexes of transition metals. The paper deals mainly with results in this field obtained in the Reviewer's laboratory. It will not be concerned with methods for the preparation of organometallic compounds of transition metals or their specific properties.

II. POLYMERISATION OF DIENES BY ORGANIC COMPOUNDS OF TRANSITION METALS

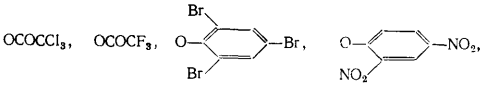
Ziegler–Natta systems, comprising mainly organoaluminium compounds and salts of transition metals, have found wide application in industry for the production of stereoregular polymers of alkenes and dienes. An immense number of scientific papers, reviews, and patents have been devoted to these questions. We shall dwell only briefly on the composition of the principal types of systems employed for the stereospecific polymerisation of dienes, and examine certain secondary reactions in the polymer chain leading to disruption of the chain structure.

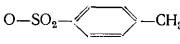
cis-Polyisoprene, similar in structure and properties to natural rubber, was obtained[1,2] by means of the classic Ziegler system comprising triethylaluminium and titanium tetrachloride. Various modifications of the system, containing titanium tetrachloride, have since been employed for the industrial production of *cis*-polyisoprene. This system proved insufficiently stereospecific for butadiene.[3] Later investigations have shown that systems containing titanium tetraiodide or mixed halides of titanium increase the content of *cis*-butadiene units[4-6] to 90–95%. Systems consisting of an alkylaluminium halide and a cobalt or nickel salt have also been used to obtain *cis*-polybutadiene.[7-12] Crystalline *trans*-polybutadiene and *trans*-polyisoprene were obtained in the presence of organoaluminium compounds and vanadium halides[13,14] and of higher oxides of chromium deposited on aluminium silicate[15]. Systems based on organoaluminium compounds and a tetra-alkoxytitanium or cobaltous chloride yield stereoregular 1,2-polybutadiene and 3,4-polyisoprene[12,16-19].

Ziegler–Natta systems have been used to obtain *cis*- and *trans*-polypentadienes[20,21], alternating butadiene–propene copolymers[22,23], and several other stereoregular polymers and copolymers of dienes. Many of these systems contain additional components (water, ketones, ethers, esters, Lewis acids, etc.) enhancing their efficiency and stereospecificity of action. As research into the mechanism of the action of the various systems intensified, it became increasingly obvious that the transition metals were the main factor in Ziegler catalysis, and that chain growth occurred at the bond attaching the transition metal to a carbon atom. However, the composition of the systems was too complicated for direct experimental studies of the nature of the active centres and the mechanism of stereoregulation. The most promising approach was to use individual organic compounds of transition metals, so that a direct relation could be established between the nature of the active centres and their stereospecificity. The wide range of action of such compounds is due to the possibility of varying the state of oxidation of the metal and the chemical nature of the ligands surrounding it.

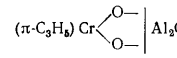
During recent years stable, hydrocarbon-soluble σ- and π-allyl compounds of various transition metals—titanium(IV and III), nickel(II), chromium(III and II), molybdenum(IV), vanadium(III), iron(III), and manganese(II)—and the derivatives listed below

1. $(\pi\text{-}C_5H_9)_3Ti$, $[(CH_3)_3SiCH_2]_3Ti$, $\left(\pi\text{-}\bigcirc\right)_3Ti$;
2. $[(CH_3)_3SiCH_2]_4Ti$, $[(CH_3)_3SiCH_2]TiCl_3$, $[(CH_3)_3SiCH_2]_2TiCl_2$;
3. $(C_6H_5CH_2)_4Ti$, $(C_6H_5CH_2)_3TiX$ (X=Cl, Br, I)
4. π-RNiX (R=C_3H_5, C_4H_7, C_5H_9, , X=Cl, Br, I,





5. $(\pi\text{-}C_3H_5)_3Cr$, $(\pi\text{-}C_5H_9)_3Cr$, $(\pi\text{-}C_3H_5)_2Cr{-}O{-}|SiO_2$,
$(\pi\text{-}C_5H_9)_2Cr{-}O{-}|SiO_2$, $(\pi\text{-}C_5H_9)_2Cr$;



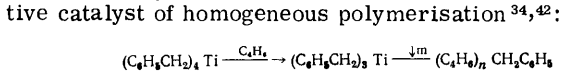
6. $(\pi\text{-}C_5H_9)_3Co$, $(\pi\text{-}C_5H_9)_3Fe$, $(\pi\text{-}C_5H_9)_2Mn$,
$(\pi\text{-}C_5H_9)_3V$;

7. $(\pi\text{-}C_3H_5)_4Mo$, $(\pi\text{-}C_3H_5)_3MoX$ (X = Cl, Br, I, $OCOCCl_3$),
$(\pi\text{-}C_5H_5)_4W$ and its derivatives

have been prepared in our laboratory[24-41], most of them for the first time. Compounds in groups 1 and 2, π-pentenyl and π-cyclohexenyl complexes of nickel, and especially π-allyl complexes of chromium chemically combined with silicon dioxide (group 5), were the most stable at 20–50°C. Examination of the catalytic activity and the stereospecificity of action of several individual organometallic compounds permitted a direct study of the nature of the active centres effecting a particular type of stereoregulation.

1. Organotitanium(IV) Compounds

Tetrabenzyltitanium in an aromatic solvent is an effective catalyst of homogeneous polymerisation[34,42]:



(A)

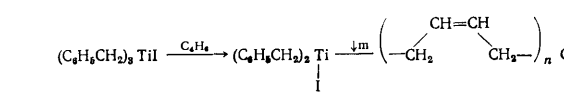
↓ m — point of entry of monomer (m).

The active centre (A) retains three benzyl groups and one growing polymer chain at various degrees of polymerisation[42,43]. Titanium remains in the quadrivalent state, which indicates that the organometallic compound is quite stable up to 50°C. In the polymerisation of butadiene the polymer chain consists mainly of 1,2-units[34,42,43], but every possible type of structure (*cis*-1,4, *trans*-1,4, 3,4, and 1,2) is formed from isoprene[44].

Table 1. Stereospecificity of action of tribenzyltitanium halides and effect of donors[43,44].

Monomer	Catalytic system	Microstructure of chain, %			
		cis	*trans*	1,2-	3,4-
Butadiene	R_4Ti	20	20	60	—
	R_3TiCl	35	19	46	—
	R_3TiBr	66	13	21	—
	R_3TiI	97	0.5	2.5	—
	$R_3TiI + 10(C_2H_5)_2O$	79	17	4	—
	R_3TiI + 10 oxolan	27	14	59	—
Isoprene	R_4Ti	0	75	7	18
	R_3TiCl	19	36	6	39
	R_3TiBr	69	0	4	27
	R_3TiI	87	0	0	13
	$R_3TiI + 10(C_2H_5)_2O$	16	37	2	45
	R_3TiI + 10 oxolan	7	16	9	68

A more effective catalyst, producing ~95% of *cis*-units, is tribenzyltitanium iodide[42-44]:



(B)

The presence of the iodide anion directly at the reaction centre inverts the stereospecificity of the catalytic effect.

In the active centre (B) titanium is maintained in the quadrivalent state throughout polymerisation. These systems exhibit no fundamental differences from organometallic compounds of alkali and alkaline-earth metals, since chain growth takes place at an ordinary carbon–metal σ-bond.

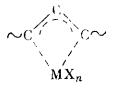
Characteristic features of benzyl derivatives of titanium(IV) will be noted below in the discussion of copolymerisation processes. Table 1 gives the chain microstructure in the polymerisation of butadiene and isoprene under the influence of various such derivatives[43,44]. The content of *cis*-1,4-units increases in the sequence

$$(C_6H_5CH_2)_4Ti < (C_6H_5CH_2)_3TiCl < (C_6H_5CH_2)_3TiBr < (C_6H_5CH_2)_3TiI.$$

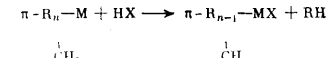
The last of these compounds is a highly selective catalyst for obtaining *cis*-polymers. Oxygen-containing solvating additives increase the content of *trans*- and 3,4-units. It is possible that the use of tribenzyltitanium iodide under especially pure conditions would have yielded only *cis*-units.

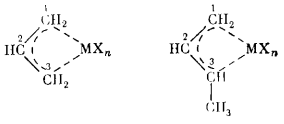
2. π-Allyl Complexes of Transition Metals

It is well known that alkyl derivatives of transition metals are extremely unstable, readily decomposing at the instant of formation[45]. The greater stability of the π-allyl complexes is due to donor–dative interaction involving π-electrons of the double bond and non-bonded *d*-electrons of the transition metal[46,47]. π-Allyl complexes of metals of general formula

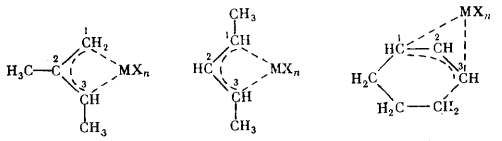


represent most closely the structures of the terminal units in an active centre during the polymerisation of dienes, so that study of the specific reactions of such complexes under model conditions is of considerable interest for an understanding of the mechanism of polymerisation: *anti*- and *syn*-configurations of the π-allyl complexes correspond to *cis*- and *trans*-states of the terminal growing unit. Organomagnesium synthesis in ethereal medium leads to the formation of poly-π-allyl derivatives π-R_nM, from which exchange with acids and other compounds yields[27,28,48,49] the corresponding derivatives:





(I) (II)



(III) (IV) (V)

The allyl complexes (I), (IV), and (V) are characterised by equivalence of the two carbon–metal bonds and by higher stability, especially complexes (IV) and (V), containing alkyl substituents on the atoms at positions 1 and 3.

Several of the pentenyl complexes of titanium(III), cobalt(III), vanadium(III), chromium(III), iron(II), and manganese(II) synthesised in the Laboratory of Organometallic Catalysis at the Institute of Petrochemical Synthesis of the USSR Academy of Sciences have proved to be stable in solution at room temperature for a long time[24,25,29]. Compounds of type (II) correspond to the growing chain unit of polybutadiene, those of type (III) to the most probable conformation of an isoprene active centre, and (IV) and (V) to pentadiene and cyclohexadiene active centres respectively.

Allyl-, but-2-enyl-, pentenyl-, and cyclohexenylnickel halides have been prepared[50] from the corresponding alkenyl halides and nickel carbonyl:

$$RHal + Ni(CO)_4 \rightarrow RNiHal \ .$$

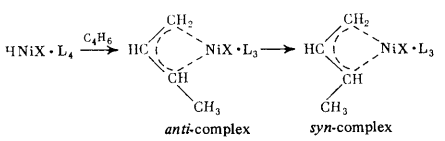
Several specific reactions characteristic of π-allyl complexes

$$(\pi\text{-}RNiX)_2 \underset{H_2O,\,oxolan}{\overset{a}{\rightleftharpoons}} \pi\text{-}R_2Ni + \pi\text{-}RNiX \cdot NiX_2$$
$$\downarrow b \qquad\qquad c \downarrow C_4H_6$$
$$R\text{—}R \qquad\qquad Ni + R\text{—}R$$

are of interest for understanding the chemical reactions involved in polymerisation. In the presence of water or oxolan an equilibrium is established (reaction *a*), which can be displaced to the right[51] by distilling off π-R_2Ni from the system. Reaction (*b*), accompanied by formation of the recombination product R–R, takes place under the influence of various electron-accepting components, especially in aromatic solvents[52,53]. Reaction (*c*) occurs[54] in the presence of dienes with the formation of "bare" active nickel, a catalyst for the cyclic oligomerisation of dienes. Reactions (*b*) and (*c*) illustrate the possibility of the destruction of active centres by recombination during stereospecific polymerisation. This is probably why attack on a growing polymer centre by CH_3O^3H and $^{14}CH_3OH$ in several cases does not result in the appearance of radioactivity in the polymer[55]. The decomposition of π-but-2-enylnickel chloride by acids leads to the formation of but-1-ene, but hydrogenolysis (and alkaline decomposition) yield *trans*-but-2-ene [56–58]:

$$\pi\text{-}C_4H_7NiX \begin{cases} \xrightarrow{HCl\,(H_2SO_4)} CH_3CH(NiX)\text{—}CH_2 \rightarrow \text{but-1-ene (90\%)} \\ \xrightarrow{H_2} CH_3CH{=}CH\text{—}CH_2NiX \rightarrow \textit{trans}\text{-but-2-ene (96\%)} \end{cases} .$$

The point of attack and the nature of the "units" formed [but-1(or 2)-ene] depend on the nature of the reagent. Extremely important results were obtained in work[59] showing that the primary addition of butadiene at a hydrogen–nickel bond results in formation of an anti-complex, which then isomerises into the *syn*-complex:



X = sulpho; L = phosphite ligand .

(*a*) Organochromium compounds

Tris-π-allyl compounds of chromium catalyse the polymerisation of dienes in hydrocarbon solutions[60,61]. All three alkenyl groups are involved in steps of chain growth:

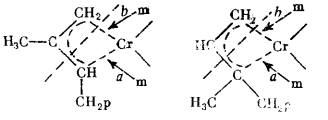
$$\pi\text{-}R_3Cr + 3n\,C_4H_6 \rightarrow [\pi\text{-}R(C_4H_6)_n]_3Cr \ .$$

Three polymer chains are formed on one chromium atom. The resulting polymers have low molecular weights owing to chain transfer to the monomer:

$$RCH_2\text{—}CH(CH{=}CH_2)\text{—}Cr\langle + C_4H_6 \rightarrow R\text{—}CH{=}CH\text{—}CH{=}CH_2 + \pi\text{-}C_4H_7Cr\langle \ .$$

Every "dead" polymer molecule contains a conjugated group of double bonds at the end of the chain.

The butadiene chain contains ~80% of 1,2-units. Every possible type of unit arises in the polymerisation of isoprene. The formation of roughly the same quantities of vinyl and isoprenyl side-groups in polyisoprene (1,2 and 3,4-units) evidently indicates that the two types of centres



are equally probable, where *a* is the point of entry of the monomer into the chain at a carbon–chromium σ-bond with formation of 1,2- and 3,4-units, while *b* is the point of entry of the monomer on formation of 1,4- and 4,1-units. Hence 1,4-units are randomly arranged "head to tail" in the polyisoprene chain. The polymerisation of isoprene under the influence of $(\pi\text{-}C_5H_9)_2Cr$ in hydrocarbon solution yields a polymer containing only 1,2- and 3,4-units (in roughly equal quantities)[29]. Entry of monomer into the chain is accomplished only by path *a*.

When tris-π-allylchromium interacts with vacuum-ignited aluminium silicate, silica gel, or aluminium oxide, the organometallic compound passes quantitatively from solution to the surface[30,31]:

$$\pi\text{-}R_3Cr + HO\text{—}|SiO_2 \rightarrow \underset{R}{\overset{R}{>}}Cr\text{—}O\text{—}|SiO_2 + RH \qquad (A)$$

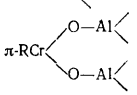
$$\pi\text{-}R_3Cr + \begin{matrix} HO\text{—} \\ HO\text{—} \end{matrix}\Big|Al_2O_3 \rightarrow RCr\langle\begin{matrix} O\text{—} \\ O\text{—} \end{matrix}\Big|Al_2O_3 + 2RH \qquad (B) \ .$$

The reaction with aluminium silicate results in the separation of one RH molecule and the formation of an active centre (A) in which two alkenyl groups are retained by one chromium atom. An important feature is that, in contrast to the initial tris-compound, the new organochromium compound is extremely stable when kept at room temperature for a long time. Since this catalyst causes also the polymerisation of alkenes, it can reasonably be assumed that the σ-state of the chromium–carbon bond is more characteristic of this organochromium compound. This catalyst was highly stereospecific for the synthesis of *trans*-polyisoprene and *trans*-polybutadiene. Because of the great stability of chromium–carbon bonds, polymerisation takes place by a mechanism of "live" chains without destruction of active centres. Two polymer chains are formed on one chromium atom, with continuous increase in molecular weight with the degree of polymerisation. The reaction of the tris-compound with aluminium oxide produces an active centre (B) in which one carbon–chromium bond is preserved at the chromium atom. In the polymerisation of butadiene and isoprene this catalyst yields polymers containing 92–93% of *cis*-units.

It has thus been shown for chromium compounds that, depending on the electronic state of the transition metal

and the nature of the ligands surrounding it, all kinds of microstructures can be realised with great selectivity on the same metal atom. This principal, which is probably common to many transition metals, has been confirmed for compounds of titanium, niobium, cobalt, and nickel. Although the compounds π-R_3Cr, π-R_3Nb, π-R_3Co, etc. behave in exchange reactions as molecules containing the metal in the tervalent state, the latter is in effect present in a more reduced state, in view of its greater electronic saturation in π-allyl complexes. This principle is consistent with several specific reactions of poly-π-allyl complexes that are typical of zerovalent metals. In this sense the transitions π-$R_3M \rightarrow \pi$-$R_2MX \rightarrow \pi$-RMX_2 can be regarded as oxidation accompanied by increase in the positive charge on the metal atom, although the exchange equivalent remains unchanged. The systems become *cis*-stereoregulating after one or two alkenyl groups have been replaced by electronegative ligands (Table 1A).

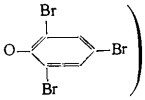
Table 1A.

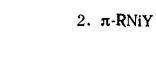
Catalyst	Chain microstructure
π-R_3Cr	81% 1.2-[48,60,61]
π-R_3Nb	100% 1.2-[48]
π-$R_2CrOSi\equiv$	96% *trans*-[30,31]
	93% *cis*-[30,31]
π-$RCrCl_2$	93% *cis*-[49,60,61]
π-$R_2CrOCOCCl_3$	93% *cis*-[48,60,61]
π-R_2NbCl	91% *cis*-[48]

Higher oxides of chromium (CrO_3) on aluminium silicate have long been known as catalysts for the polymerisation of alkenes. Their catalytic action was earlier attributed to the presence of Cr^{4+}, Cr^{5+}, and Cr^{6+}. Detailed investigation of this system [30,31,62] has shown that the active centre effecting polymerisation is identical with the centre (A) obtained in the reaction of π-R_2Cr with aluminium silicate: i.e. chromium is present in the active centre in a more reduced state than Cr^{3+}. In both cases polymerisation takes place by a mechanism of "live" chains with the formation of *trans*-units, and values of the copolymerisation constants r_1 and r_2 for the pair butadiene–isoprene fully coincide.

(*b*) Organonickel compounds

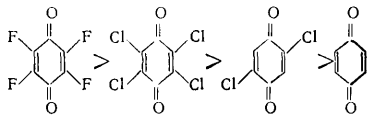
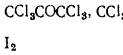
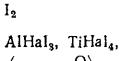
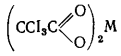
Research on the use of organonickel compounds for the stereospecific polymerisation of dienes has been published in many papers and reviews [63-65]. We shall consider only a few of the most important results of interest in connection with the mechanism of stereoregulation. The compounds π-RNiX catalyse the polymerisation of dienes in solution. The nature of the anion X has a significant influence on the stereospecificity of the catalytic effect:

1. π-RNiX (X=I, Br, Cl, O-) → Crystalline *trans*-polymers of butadiene and isoprene (Refs. 27, 28, 66-71),

2. π-RNiY (Y=$OCOCCl_3$, $OCOCF_3$, O-) → *cis*-Polybutadiene (Refs. 27, 28, 72).

Replacement of X by more electronegative ligands leads to a significant enhancement of the catalytic activity of the system and to a reversal of the stereospecificity. However, systems based on complexes of π-RNiCl with various electron-accepting compounds proved to be the most effective and *cis*-stereoselective (Table 2). [63,73-77]

Table 2. Complexes of alkenylnickel halides with electron acceptors.

Complex	Electron-accepting compound (A)
π-$R\overset{(+)}{N}iCl$(Br, I) ⋮ $A^{(-)}$	
(charge transfer complexes)	CCl_3COCCl_3, , , CCl_3COOH, CF_3COOH, I_2
π-$RNi^{(+)}[ClA]^{(-)}$ (anion-transfer complexes)	$AlHal_3$, $TiHal_4$, $SnHal_4$, $ZnHal_2$, $CoHal_2$, 

Charge-transfer complexes are formed with the aid of halogenoquinones, whose effectiveness is consistent with the redox potential of the quinones, halogenated carbonyl compounds, halogenated acids, etc. Anion-transfer complexes (such as ion-pairs) are formed by various Lewis acids. The reversal of stereospecificity on passing from π-RNiI to the π-RNiI–I_2 system indicates directly that the effect is not due to replacement of ligands but to increase in the positive charge on the nickel atom.

Table 3. Catalytic system and structure of polybutadiene.

Catalytic system	Chain microstructure, %			$[\eta]$, dl g^{-1}	Physical state of polymer	Ref.
	1,2-	*cis*-	*trans*-			
π-R_3MoCl	90	2	8	3.1	amorphous	37
π-$R_3MoOCOCCl_3$	97	—	3	3.0	amorphous	37–39
π-$R_4Mo + CCl_3COCl$	95	—	5	6.5	amorphous	38,39
π-R_4Mo + chloranil	95	—	5	5.4	amorphous	38,39
π-$R_4Mo + C_3H_5I$	96	—	4	2.0	crystalline	40
π-$R_4W + C_3H_5Cl$(I)	95 0	—	5.0		amorphous	41
π-$R_4W + O_2$	99 5	—	0.5		amorphous	41

Kinetic investigation of various nickel systems has thus far revealed a fractional order (0.5) with respect to the catalyst only for $(\pi\text{-RNiX})_2$, where X = I, Br, Cl, which indicates that polymerisation involves only a small quantity of monomeric forms in equilibrium with the main, inactive dimeric form [70,71]. The kinetic orders with respect to the catalyst established in *cis*-regulating systems, at least in the case of π-$RNiOCOCF_3$ and complexes with electron acceptors, indicated that the organonickel centres were fully involved in steps of chain growth [27,28,56,57,78].

(*c*) Organomolybdenum and organotungsten compounds

Organometallic compounds based on tetra-π-allylmolybdenum are highly effective catalysts for the production of amorphous and crystalline 1,2-polybutadiene [37-40] (Table 3). The high intrinsic viscosity of the polymer indicates the formation of a very small quantity of long-lived active centres. Detailed study of the π-R_4Mo + $CH_2:CHCH_2I$ system, which forms crystalline 1,2-polybutadiene, has shown that the active centre is the compound π-$R_2Mo(I)$-p, which results from the interaction of the above components. Chain growth occurs at the allylmolybdenum σ-bond, but transition of the σ-bond into the stable π-allyl form is an act of chain termination[37-40].

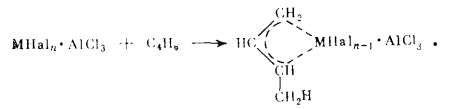
As is shown in Table 3, systems based on π-allyl derivatives of tungsten also effect 1,2-stereoregulation[41].

3. Formation of Organometallic Compounds during Polymerisation

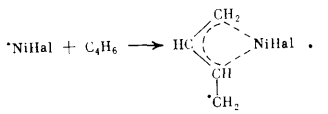
Transition-metal compounds of the π-allyl type are formed as a result of diverse reactions because of their relatively high stability. Metal hydrides in the presence of butadiene are converted into the corresponding π-but-2-enyl complexes, as was proved [79,80] with nickel, cobalt, and chromium:

$$NiH_2 + C_4H_6 \rightarrow (\pi\text{-}C_4H_7)_2Ni\ ,$$
$$CoH_2 + C_4H_6 \rightarrow (\pi\text{-}C_4H_7)_nCo\ ,$$
$$CrH_3 + C_4H_6 \rightarrow (\pi\text{-}C_4H_7)_3Cr\ .$$

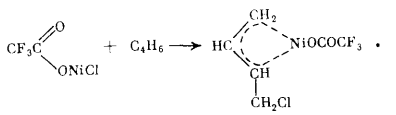
Complexes of halides of transition metals (nickel, cobalt, vanadium) with aluminium chloride cause the stereospecific polymerisation of dienes, presumably [81,82] by the reaction



Defect halide salts (subhalides) of nickel, cobalt, and niobium, obtained by heating in a vacuum, effect the polymerisation of dienes with the stereospecificity characteristic of the corresponding π-allyl complexes. It has been proved for nickel halides that formation of an organometallic active centre involves an intermediate radical-ion stage [83-85]:



Mixed salts react with dienes in several cases with the formation of π-allyl active centres [86]:



When $CF_3COONi^{36}Cl$ is used, the labelled chlorine atom is incorporated into the polymer chain [87].

In Ziegler catalysis organic compounds of transition metals are formed by exchange reactions with aluminium alkyls:

$$MX_n + R_3Al \rightarrow RMX_{n-1} + R_2AlX\ ,$$
$$MX_n + R_2AlCl \rightarrow RMX_{n-1} + RAlClX\ .$$

Addition of a diene at the alkyl–metal bond tends to stabilise the resulting organometallic compound as a π-allyl complex. With titanium(IV) halides a π-allyl active centre can be formed only after reduction to titanium(III). The alkylaluminium halides probably act subsequently as electron acceptors, forming complexes with RMX_{n-1} and enhancing their effectiveness and stereospecificity, as was established above for π-allyl complexes of nickel.

4. Nature of Secondary Reactions in Polymer chains during Stereospecific Polymerisation of Dienes by Ziegler Systems

The Ziegler–Natta catalytic systems employed for the stereospecific polymerisation of dienes consist of organoaluminium compounds and halides of transition metals, mainly titanium, nickel, and cobalt. With the first of these metals appearance of the catalytic complex is preceded by reduction of the tetrahalide to the trihalide accompanied by formation of R_2AlHal:

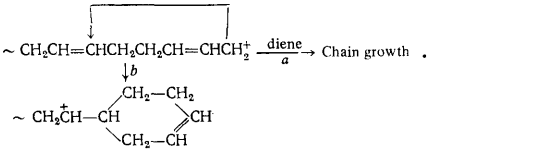
$$R_3Al + TiHal_4 \rightarrow R_2AlHal + RTiHal_3\ ,$$
$$RTiHal_3 \rightarrow {}^1/_2R_{-H} + {}^1/_2R_{+H} + TiHal_3\ .$$

Under certain conditions alkylaluminium halides and titanium(IV) chloride are catalysts for cationic processes. In catalytic systems based on nickel and cobalt halides the alkylaluminium halides and water are used in the molar proportions

$$NiCl_2\ (CoCl_2) : R_2AlCl : H_2O = 1 : 150 : 10$$

In such cases the initial catalytic system is characterised by extremely high cationic activity, as is illustrated by the possible use of its components ($R_2AlCl + H_2O$) to initiate the polymerisation of isobutene [88]. The organometallic active centres that effect the stereospecific polymerisation of dienes are capable of initiating the oligomerisation and polymerisation of alkenes, which indicates the theoretical possibility that double bonds of the polymer chain are involved. The most important results of investigations on these aspects are reported below.

In anionic and coordination polymerisation conjugated dienes are considerably more reactive than the corresponding alkenes. A distinguishing feature of cationic systems is the comparatively small differences in reactivity between dienes and alkenes [89-91]. Thus isopentene (m_1) is more reactive than butadiene (m_2) on cationic copolymerisation: $r_1 = 0.90$ and $r_2 = 0.38$



Because of the great probability of reaction (*b*) cyclised polymers, less unsaturated than would be expected theoretically, are formed even at low degrees of conversion in the cationic polymerisation of dienes. In dilute solutions of natural rubber and *cis*-polybutadiene intramolecular cyclisation takes place under the influence of the R_2AlCl–H_2O system, accompanied by diminution of unsaturation with maintenance of the molecular weights of the polymers [92-94].

It was shown for the model compound 3-methylpent-2-ene [95] that the cation-active components of Ziegler systems initiate the *cis–trans* isomerisation of isoprene

units extremely efficiently (Table 4). Analogous isomerisation effects were observed[92,96,97] in benzene solutions of natural rubber under the influence of ethylaluminium dichloride, diethylaluminium monochloride, and titanium tetrachloride; the coactivators in such processes were traces of water and other compounds.

Table 4. Variation in composition of reaction mixture and structure of 3-methylpent-2-ene (at 60°C).

Catalyst (mole % on monomer)	Продолжительность реакции, мин	Isolated, % on initial		Monomer structure, %	
		monomer (C_6)	dimer (C_{12})	*cis*	*trans*
$C_2H_5AlCl_2$ (3.6%)	0	100	—	86	14
	25	68	—	70	30
	60	54	46	60	40
	90	—	—	48	52
$TiCl_4$ (2.5%)	8	79	21	66	34
	60	46	54	52	48
Equilibrium	—	—	—	42.2	57.8

Reactions of a third type occurring under the influence of cationic initiators involved the migration of double bonds in the polymer chain. Such migration takes place in polybutadiene in the presence of titanium tetrachloride and alkylaluminium chlorides[92], until conjugated systems are formed:

$$\sim CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2\sim \xrightarrow{+H^+} \sim CH_2CH_2\overset{+}{C}HCH_2CH_2CH{=}CHCH_2 \sim \xrightarrow{-H^+}$$
$$\rightarrow \sim CH_2CH_2CH{=}CHCH_2CH{=}CHCH_2\sim \xrightarrow{+H^+}$$
$$\rightarrow \sim CH_2CH_2CH_2\overset{+}{C}HCH_2CH{=}CHCH_2 \sim \xrightarrow{-H^+} \sim CH_2CH_2CH_2CH{=}CH{-}CH{=}CHCH_2 \sim .$$

A detailed study of these reactions has been made[98].

Nuclear magnetic resonance spectroscopy of the *cis*-polybutadiene obtained in the presence of the R_2AlCl–$CoCl_2$ system showed the presence of : CH.CH_2.CH : groups, which characterise the first stage in the migration of double bonds[99].

Research showed the usefulness of introducing into the catalytic systems components that inhibit the development of cationic processes. Such inhibitors may be weak Lewis bases, which do not affect the rate of polymerisation, the molecular weight, or the chain microstructure in the stereospecific polymerisation of butadiene, as was shown for diphenyl ether[100].

In the absence of the monomer (a conjugated diene) migration and isomerisation of double bonds can be effected in model hydrocarbons and in polybutadiene not only by Ziegler systems containing cation-active components but also by organometallic complexes, active centres for stereospecific polymerisation. Thus at room temperature π-allyl complexes of nickel of general formula π-RNiHal effect[101,102] the chain isomerisation of hexa-1,5-diene

$$\underset{(A)}{CH_2{=}CHCH_2CH_2CH{=}CH_2} \rightarrow \underset{(B)}{CH_3CH{=}CHCH_2CH{=}CH_2} \rightarrow \underset{(C)}{CH_3CH{=}CH{-}CH{=}CHCH_3}$$

which involves the successive addition and detachment of HNiHal at the double bond. Migration of the double bond (A) → (B) is accompanied by the formation of *cis*–*trans* isomers and by the dimerisation of hexa-1,5-diene, which also involves addition of the organonickel compound at the double bond in the alkene. At room temperature the π-but-2-enylnickel chloride–chloroanil complex—an effective stereospecific catalyst for the production of *cis*-polybutadiene—causes the isomerisation of but-1-ene and but-2-ene into the equilibrium mixture[103].

Addition of an organometallic active centre at a double bond in the chain during the polymerisation of dienes should lead to the formation of branched polymers. The probability of such reactions is small, for conjugated dienes are considerably more reactive than alkenes in coordinated systems. The appearance of conjugated double bonds in a polymer chain as a consequence of acts of migration is probably one of the main reasons for the formation of branched polymers in the polymerisation of butadiene under the influence of a "cobalt" catalytic system. This system is characterised by very small differences in reactivity between butadiene and its alkyl derivatives (isoprene and 2,3-dimethylbutadiene),[104–106] and the "polymeric" diene formed may be actively involved in copolymerisation with butadiene. It has been demonstrated for cobalt, nickel, and chromium catalytic systems that the main reaction limiting chain growth is chain transfer to the monomer:

$$\sim \pi\text{-}CH_2CH{=}CHCH_2{-}MX_n \xrightarrow[a]{C_4H_6} \text{Chain growth}$$
$$b\downarrow C_4H_6$$
$$\sim CH{=}CH{-}CH{=}CH_2 + \pi\text{-}C_4H_7MX_n \xrightarrow{C_4H_6} \text{Chain growth} .$$

Reaction (*b*) is accompanied by the formation of polymer molecules containing a conjugated system of double bonds at the ends of the chains[60,61,107], whose involvement in polymerisation results in branched macromolecules.

5. Some Aspects of Copolymerisation in Coordination Systems and the Effect of Solvating Additives

On copolymerisation under the influence of RLi in hydrocarbon media dienes are considerably more reactive[108–111] than is styrene ($r_1 \gg r_2$). When the same monomers undergo copolymerisation in the presence of RLi in the usual solvating media or of organo-potassium and -sodium compounds in any media, under conditions leading to formation of 1,2- and 3,4-units, styrene has proved to be considerably more reactive[112,113] than dienes. Both phenomena (change in microstructure and reversal of reactivity) are genetically related to enhancement of the polarity of the carbon–metal bond. With compounds of transition metals, independently of the character of the stereoregulation, dienes are always considerably more reactive than styrene (Table 5).

Table 5. Relative reactivities of butadiene (m_1) and styrene (m_2) and the chain microstructure.

Catalytic system	Copolymerisation constants		Chain microstructure, %			Ref.
	r_1	r_2	*cis*-1,4	*trans*-1,4	1,2-	
RLi in oxolan	0.20	8.0	0	9	91	114
RLi in diethyl ether	0.11	1.78	—	—	—	114
RLi in toluene	15.0	0.05	44	48	8	109
π-RNiCl–Acceptor	4.6	0.13	92	6	2	115
$(\pi\text{-}C_3H_5)_4Mo$–Acceptor	27.5	0,02	4	5	91	116, 117
$(\pi\text{-}C_3H_5)_4W$–Acceptor	10.1	0.2	0	9	91	116, 117
$(\pi\text{-}C_3H_5)_4Zr$	34	0.02	61	4	35	116, 117
$(C_6H_5CH_2)_4Ti$	27	0 02	15	25	60	116, 117

The results indicate a coordination mechanism for the formation of any type of unit on a transition metal. π-Allyl active centres are considerably more stable than the corresponding styrene derivatives. Entry of styrene into

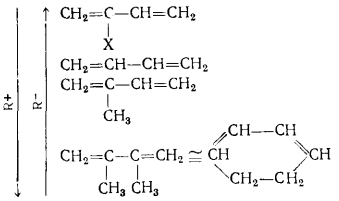
Table 6. Values of r_1 and r_2 in the copolymerisation of dienes in hydrocarbon media.

Catalytic system	Butadiene (m_1), isoprene (m_2)			Butadiene (m_1), 2,3-dimethylbutadiene (m_2)			Butadiene (m_1), cyclohexadiene (m_2)			Butadiene (m_1), penta-1,3-diene (m_2)		
	r_1	r_2	Ref.	r_1	r_2	Ref.	r_1	r_2	Ref.	r_1	r_2	Ref.
$R_3Al—TiCl_4$	1.0	1.0	104—106, 118, 119	2.16	0.39	126						
$R_3Al—TiI_4$	1.9	0.5	120									
$R_3Al—TiI_4$	2.8	0.53	121, 122	6.3	0.15	121				2.6	0.5	121, 122
$R_2AlCl—CoCl_2$	0.9	1 3	123	2.7	1.1	126						
$R_2AlCl—CoCl_2$	2.3	1.15	104—106									
$R_2AlCl—CoCl_2$	1.0	0.9	121, 122	0.74	0.67	121, 122				1.2	0.3	121, 122
$R_2AlCl—NiCl_2$	1.15	0.59	123									
π-RNiX — Acceptor	6.2	1.1	121, 122	2.8	0.18	127	0.4	0.9	36			
$(π\text{-RNiI})_2$	0.3	2.35	124				0.8	1.1	127			
$π\text{-R}_2Cr—O—$ | Aluminium silicate	1.06	0.8	125									
CrO_3 — Aluminium silicate	1.04	0.70	125									
RLi	3.38	0.47	110—111									

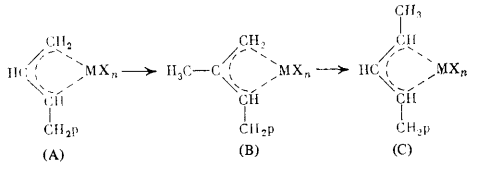
a chain therefore involves a sharp decrease in molecular weight owing to chain-transfer reactions [115]

$$—CH_2—\underset{\displaystyle C_6H_5}{\underset{|}{CH}}—NiX + C_4H_6 \rightarrow —\underset{\displaystyle C_6H_5}{\underset{|}{CH}}=CH + π\text{-}C_4H_7NiX \ .$$

With respect to relative activity on ionic copolymerisation dienes form the well known sequence



in which X is an electronegative substituent. This sequence breaks down with systems in which the stage of coordination of the diene with the transition metal begins to play a significant part. Table 6 gives data on copolymerisation constants of dienes in various systems. In most cases butadiene is more active than alkylated dienes, which is typical of anionic active centres, but $r_1 = r_2$ in several systems ($R_3Al–TiCl_4$, $R_2AlCl–CoCl_2$, and "chromium" systems) or even $r_2 > r_1$ in the copolymerisation of butadiene with cyclohexadiene effected by π-allyl complexes of nickel. Passage from a butadienyl (A) to an isoprenyl (B) and especially a pentadienyl (C) π-allyl centre



(A) (B) (C)

is extremely advantageous, since the stability of the organometallic compound increases in this sequence. Low values of r_2 for pentadiene and isoprene on copolymerisation with butadiene indicate that steric factors in the stage of coordination of the monomer on the transition metal are probably of decisive importance for the reactivity.

The most interesting feature of copolymerisation in coordination systems is the mutual influence of monomers on the character of the stereoregulation. This phenomenon, observed by many workers [104–106,121,122,128] and directly connected with the nature of the active centres and the mechanism of formation of units in them, can be illustrated by a few examples (Table 7). In the $R_2AlCl–CoCl_2$ system the entry of alkylated butadiene derivatives into the chain

Table 7. Microstructure of butadiene units in copolymers[121].

Catalytic system	Second monomer (m2)	Copolymer m_2, mole %	Microstructure of butadiene part of chain, %		
			cis-1,4	*trans*-1,4	1,2-
$R_2AlCl—CoCl_2$	isoprene	0	94	3	3
	isoprene	32	75	7	18
	isoprene	53	58	3	39
	2,3-dimethylbutadiene	27	44	7	49
	2,3-dimethylbutadiene	41	26	6	68
	penta-1,3-diene	41	*	*	20
	penta-1,3-diene	53	*	*	50
$R_3Al—TiI_4$	isoprene	0	90	6	4
	isoprene	31	49	37	12
	isoprene	66	41	40	14
	2,3-dimethylbutadiene	35	76	19	5
$(π\text{-RNiCl})_2 \cdot TiCl_4$	isoprene	0	90	8	2
	isoprene	10	77	19	4
	isoprene	26	71	24	5
	isoprene	68	50	39	11

*The remainders are the sums of *cis*-1,4 and *trans*-1,4 units.

is accompanied by a corresponding increase in the proportion of 1,2-butadiene units instead of the *cis*-units characteristic of a butadiene homopolymer. A decrease is observed in the number of 3,4-isoprene units relative to polyisoprene obtained on the same catalyt[104–106,121,128]. Hence linking butadiene and isoprene units in the copolymer have the structure

$$—CH_2—\underset{\displaystyle CH_2}{\underset{\|}{CH}}—CH_2—CH=\underset{\displaystyle CH_3}{\underset{|}{C}}—CH_2— \ .$$

In the $R_3Al–TiI_4$, $R_3Al–TiI_2Cl_2$, and π-RNiX–Acceptor systems the same monomers convert the *cis*-butadiene units predominantly into *trans*-units. Similar effects are produced by electron-donating additives (ethers, esters, sulphides, amines) in the homopolymerisation of butadiene. In the $R_2AlCl–CoCl_2$ system they cause an increase in the number of 1,2-units, but in the other systems they increase the quantity of *trans*-units [129–136].

Chromium-containing systems enable stereoregular *trans*-copolymers of butadiene and isoprene to be obtained in which the structure of the units in the homopolymers is preserved. With *cis*-regulating nickel systems statistical *cis*-copolymers of butadiene and cyclohexadiene can be obtained, for which pair of monomers [36] $r_2 > r_1$.

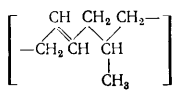
As noted above, oxygen-containing compounds increase considerably the content of 3,4-, 1,2-, and *trans*-units in the polymerisation of butadiene and isoprene under the influence of organotitanium(IV) compounds. In most cases

the change in stereospecificity in the presence of electron-donating components is accompanied by a considerable decrease in the rate of polymerisation, probably due mainly to the equilibrium

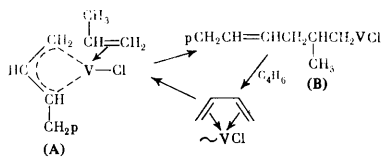
$$\overset{\text{Donor}}{\underset{\downarrow}{\text{pMX}_n}} + \text{Diene} \rightleftarrows \overset{\text{Diene}}{\underset{\downarrow}{\text{pMX}_n}} + \text{Donor} .$$

With sufficiently high concentrations of solvating components or in the case of bidentate complexing additives polymerisation ceases.

In the presence of certain oxygen-containing components at low temperatures systems containing organoaluminium compounds with vanadium and titanium halides yield[22,23] an alternating copolymer in which the butadiene units are mainly in the *trans*-configuration.



With strict alternation of butadiene and propylene units, and the same type of structure for the former, the repeating units in the main polymer chain will contain six carbon atoms instead of the four in natural rubber and in stereoregular polymers of dienes. Vanadium is assumed[22,23] to be bivalent in the active centre, and the mechanism of the process to be



In the π-allyl complex (A) vanadium retains one coordination position, which is occupied by the alkene. After the latter has entered the chain (B), bidentate coordination of the diene becomes possible. In this way a self-regulating system is established for alternation of the monomers.

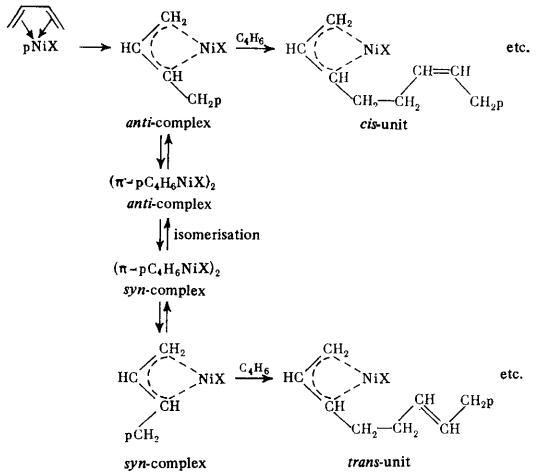
6. Mechanism of Stereoregulation

(*a*) Mechanism of formation of *cis*- and *trans*-units

As noted above, the primary addition of butadiene to HNiX yields an *anti*-complex, which then isomerises into a *syn*-complex. The hydrogenolysis of π-but-2-enylnickel chloride, obtained from but-2-enyl chloride and nickel carbonyl, forms 95% of *trans*-butene with but-1-ene completely absent[58]. Hence the content of the *syn*-form at equilibrium is close to 100%. The rate of *anti–syn* isomerisation of the complex depends, of course, on the nature of the metal and of the ligands. A diene coordinates with a transition metal always as a bidentate ligand: as a unidentate ligand it would give way to the more basic monoenes. This factor is probably decisive in the formation of alternating copolymers of dienes with alkenes: in the presence of two vacancies the diene is coordinated preferentially, but in the presence of one vacancy the alkene. The especially advantageous character of bidentate coordination is illustrated by the fact that compounds of the type $-OCH_2CH_2O-$ or $\rangle NCH_2CH_2N\langle$ on coordination polymerisation are tenfold as effective as oxolan and other solvating agents in influencing the kinetics of polymerisation and the microstructure of the chain. The considerably higher activity of conjugated dienes than of styrene in copolymerisation under the influence of transition-metal compounds and of organolithium compounds in hydrocarbon medium is due to preferential coordination of the diene. In the suggested mechanism of stereoregulation dienes are coordinated as bidentate ligands in a cisoid configuration. We shall first consider systems exhibiting a fractional kinetic order with respect to the catalyst.

The rate of polymerisation of butadiene under the influence of π-RNiHal is proportional to the square root of the catalyst concentration[70]. Hence polymerisation takes place only on the monomeric forms π-RNiHal in equilibrium with the main dimeric form $(\pi\text{-RNiHal})_2$, which is not involved in the polymerisation. A dimeric state has been demonstrated[50] for the π-allyl and π-but-2-enyl complexes π-RNiHal.

Primary entry of the diene into the active centre leads to an *anti*-complex, from which the unit is then displaced into the chain as a *cis*-unit. Processes of *anti–syn* isomerisation occur mainly in the "sleeping" dimeric associate, which is not involved in polymerisation. This probably applies also to the polymerisation of dienes under the influence of organolithium compounds in hydrocarbon solution. It is well known that alkyl derivatives of lithium are present as association complexes in hydrocarbon solution. Numerous investigations have shown[137–140] that "live" polymeric organolithium compounds are present in hydrocarbon medium as the association complexes $(pLi)_n$, where $n = 2$ for styrene and $n = 4$ for butadiene and isoprene, the rate of polymerisation being proportional to the concentration $[pLi]^{1/n}$. Hence the ligitimate conclusion was drawn that the stage of chain growth involves the monomeric form of the organolithium compound, whose proportion at equilibrium is extremely small, and that association complexes are not appreciably involved in polymerisation. Recent investigations have shown[141,142] that the microstructure of polybutadiene and polyisoprene depends on the concentration of the organolithium compound in solution, and that *cis*-stereoregulation occurs at vanishingly low concentrations of the latter (Table 8).



The degree of dissociation of the association complexes $(pLi)_n$ into the monomeric forms increases with dilution and with rise in temperature. This suggests that *cis*-units are formed only in the monomeric form pLi, but other types of units in associated forms of pLi, in which the carbon–metal bond is more strongly polarised. The autosolvation effect in association is due to enhancement of the polarity of this bond, and the participation of association complexss in polymerisation should yield structures typical of solvates of pLi with electron-donating

components. It has recently been shown[143] that the polymerisation of dienes from the vapour phase on crystalline ethyl-lithium is very slow, with preferential formation of 3,4-, 1,2-, and *trans*-units. It is therefore highly probable that stereoregulation during polymerisation in hydrocarbon media is accomplished by the scheme[144]

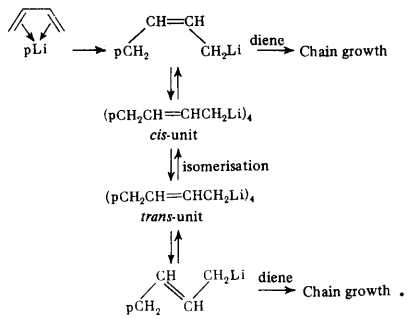
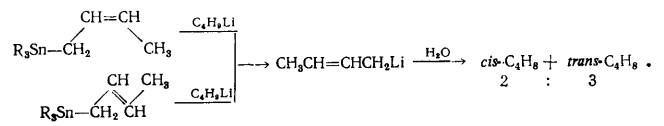


Table 8. Effect of RLi concentration on chain microstructure (in n-heptane at 20°C).

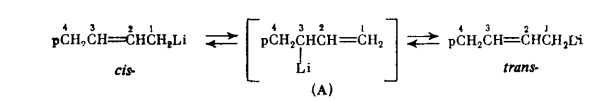
Monomer	[RLi], M	Microstructure of chain, %				Ref.
		cis	*trans*	1,2-	3,4-	
Isoprene	0.061	74	18	—	8	141
	0.001	78	17	—	5	141
	0.0001	84	11	—	5	141
	0.00008	97	—	—	3	141
Butadiene	0.073	30	46	24	—	141
	0.0124	44	46	10	—	141
	0.0003	47	45	8	—	141
	0.00054	70	28	2	—	141
	0.00001	86	10	4	—	142

Decomposition with water of but-2-enyl-lithium, formed from butyl-lithium and *cis*- or *trans*-but-2-enyltrialkyltin in ether, is a mixture of *cis*- and *trans*-butenes[145] in the proportion 2 : 3:

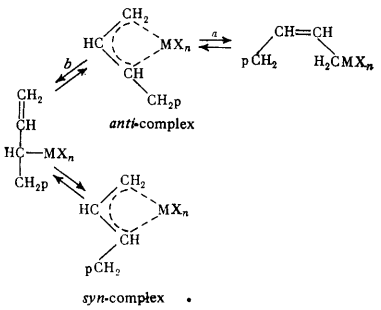


This ratio of *cis*- and *trans*-units, corresponding roughly to the composition of polybutadiene obtained under the same conditions, is probably close to the equilibrium value for the but-2-enyl-lithium–diethyl ether solvate.

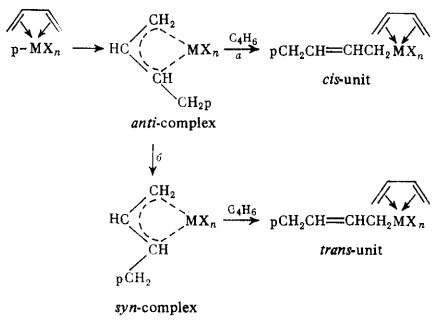
The maximum tendency to coordinate develops on the monomeric forms of pLi (and pNiX), and the diene behaves as a bidentate ligand. Primary acts of addition to the monomeric form of pLi yield a *cis*-unit, but formation of other types of structure is due mainly to isomerisation of the active centre in association complexes, although the latter may to some extent be involved in polymerisation with formation of secondary structures (3,4-, 1,2-, and *trans*-units). Isomerisation of a unit in a solvate would probably involve a stage of migration of lithium to the third carbon atom from the end of the chain



since direct *cis–trans* transitions are improbable. In association complexes lithium is able to migrate as a result of intermolecular transitions. The probability of isomerisation in solvates and aggregates increases with the polarisation of the carbon–lithium bond and the degree of charge delocalisation. A content of ~5–10% of 1,2- and 2,3-units when butadiene and isoprene are polymerised under the influence of RLi in hydrocarbon media indicates the presence of reactive structures (A) during polymerisation. An analogy exists between *cis–trans* isomerisation during anionic polymerisation and *anti–syn* transitions in π-allyl complexes of transition metals. In the latter case isomerisation can evidently take place only through $\pi-\sigma$ transitions:



The $\pi-\sigma$ equilibrium (*b*) leads to *anti–syn* isomerisation. Most catalytic systems based on compounds of transition metals are characterised by the kinetic first order of polymerisation with respect to the catalyst, and the whole of the catalyst, present mainly in the monomeric state, usually takes part in acts of chain growth. In this case the ratio of *cis*- and *trans*-units in the chain should be determined by the ratio of rates of chain growth on the active centre (reaction *a*) and of *anti–syn* (*cis–trans*) isomerisation of the active centre (reaction *b*):



Although there are at present no direct quantitative data on *anti–syn* isomerisation processss, several experimental rules are consistent with the above mechanism of stereoregulation.

(*b*) Effect of monomer concentration on chain microstructure

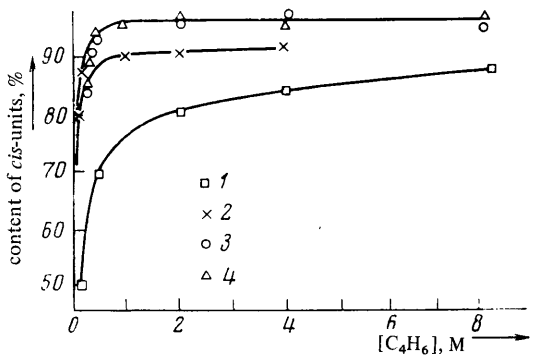
It follows from the above scheme that, in *cis*-regulating catalytic systems in which the rate of chain growth is proportional to the monomer concentration, fall in the latter should be accompanied by increase in the quantity of *trans*-units. The influence of butadiene concentration on chain microstructure has been studied[146,147] in various systems

1) $R_3Al + TiI_2Cl_2$ 2) $R_2AlCl + CoCl_2$
3) π-RNiCl · $(CCl_3COO)_2Ni$ 4) π-RNiOCOCF$_3$

characterised by first-order polymerisation with respect to the monomer. Systems (1) and (2) are of Ziegler type

and the individual organonickel compounds (3) and (4) are stereoselective for the *cis*-polymerisation of butadiene.

The diagram shows that at low monomer concentrations the quantity of *trans*-units increases considerably at the expense of *cis*-units in all cases. Such *cis–trans* conversion can be explained by variation in the relative rates of chain growth and isomerisation. In cases in which the monomer undergoing coordination affects also the rate of *anti–syn* isomerisation no relation may be observed between monomer concentration and chain microstructure.



Dependence of content of *cis*-1,4 units in polybutadiene on initial concentration of butadiene in the presence of: 1) TiI_2Cl_2 + (iso-$C_4H_9)_3Al$; 2) $CoCl_2$ + R_2AlCl; 3) π-C_5H_9. .NiCl.Ni(OCOCC$l_3)_2$; 4) π-$C_3H_5NiOCOCF_3$.

(*c*) Relative rates of chain growth in *cis*- and *trans*-regulating systems

Previous investigations in our laboratory of individual organometallic compounds—of titanium, nickel, chromium, niobium, and cobalt—have shown that all kinds of microstructures can be produced with high selectivity on the same transition metal depending on the nature of the ligands surrounding it[48,49,60,61,63]. From the suggested scheme of stereoregulation it might have been expected that on a given metal *cis*-regulating systems would generally be characterised by considerably higher rates of chain growth than would *trans*-regulating systems. Relative rates of chain growth have been compared[148] in such systems based on chromium(III), nickel(II), and titanium(IV) compounds.

The polymerisation of dienes under the influence of the active centre $R_2Cr–O–|SiO_2$, resulting from the interaction of π-R_3Cr with hydroxy-groups or ignited aluminium silicate, takes place by a mechanism of "live" chains and yields *trans*-polymers[30–32]. The molecular weight of the polymer is given by the formula $M_b = m/2n$, where m is the quantity of monomer polymerised and n the concentration of the organochromium compound. The active centre formed from π-R_3Cr and ignited aluminium oxide is a catalyst for *cis*-polymers of isoprene and butadiene. A characteristic feature of this system is the formation of products of very high molecular weight at low degrees of conversion, as a consequence of the high rate of chain growth.

Comparison of molecular weights at a low degree of conversion indicates the ratio v_a/v_b of the rates of chain growth in the systems (Table 9). Published kinetic data[43,56,57,70] have been used to calculate such ratios for nickel and titanium compounds. For systems in which the rate of polymerisation was proportional to the square root of the concentration of the transition metal it was arbitrarily assumed that the quantity of monomeric active centres was 1% of the total quantity of catalyst. Table 9 shows that with a given transition metal inversion of stereospecificity from *cis*- to *trans*-regulating is accompanied by a sharp drop in the rate of chain growth. Any factors tending to "jam" the end-group of a growing chain in an active centre entail increase in the proportion of *anti–syn* isomerisation and hence in the content of *trans*-units in the polymers.

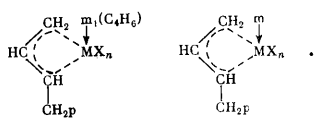
Table 9. Ratio of rates of growth in *cis*- and *trans*-regulating systems.

No.	Catalytic system	Monomer	Microstructure, %				v_a/v_b
			cis	*trans*	1,2-	3,4-	
1a	R–Cr(O–)(O–)–Al_2O_3	isoprene	95	0	0	5	~10^3
1b	R(R)Cr–O–SiO_2	isoprene	0	95	0	5	
2a	π-RNiCl·$(CCl_3COO)_2Ni$	butadiene	97	0	3	—	$7.8\cdot10^2$
2b	$(\pi\text{-RNiI})_2$, $v=k[Ni]^{0.5}$	butadiene	0	95	5	—	
3a	$(C_6H_5CH_2)_3TiI$, $v=k[Ti]^{0.5}$	butadiene	95	2	3	—	$7.4\cdot10^3$
3b	$(C_6H_5CH_2)_4Ti$	butadiene	20	20	60	—	

The inversion of stereospecificity from *cis* to *trans* under the influence of electron-donating compounds coordinated with the transition metal is evidently due to increase in the "lifetime" of the terminal unit in conformity with the equilibrium

$$\overset{\text{Donor}}{\underset{}{}}\ \ \overset{m}{\underset{}{}}$$
$$RMX_n \underset{m}{\rightleftarrows} RMX_n + \text{Donor}\ .$$

As noted above, such inversion is accompanied by a considerable decrease in the rate of polymerisation. The mutual influence of monomers on chain microstructure in coordination copolymerisation observed in several investigations can be explained, in terms of the above mechanism of stereoregulation, by variation in the rate of entry of the monomers into the chain

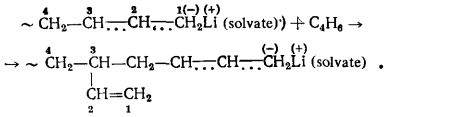


If the rate of entry of m_2 (isoprene, pentadiene, etc.) is lower than the rate of entry of butadiene, the "lifetime" of the terminal π-but-2-enyl unit is increased, as well as the probability of *anti–syn* isomerisation.

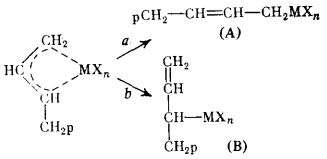
(*d*) Mechanism of formation of 1,2- and 3,4-units

Numerous investigations have established that organolithium compounds in the presence of various solvating compounds (oxolan, etc.), and organopotassium and organosodium compounds in hydrocarbon media, lead to

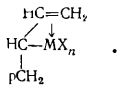
preferential formation of 1,2- and 3,4-units in the polymerisation of dienes [149-154]. Nuclear magnetic resonance spectroscopy in perdeutero-oxolan has been used [155,156] to study the charge distribution in the terminal unit of polybutadienyl-lithium and polyisoprenyl-lithium. In the absence of the monomer the charge in "live" chains is localised mainly on the terminal carbon atom. In the formation of 1,2- and 3,4-units, however, the reaction centre is established on the third carbon atom from the end of the chain:



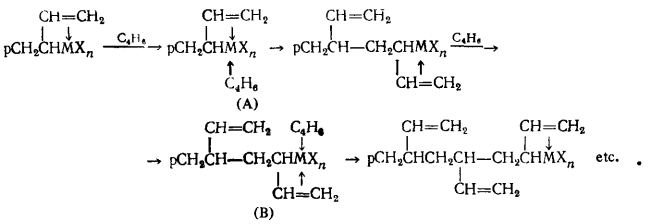
In model reactions with water, alcohol, and other compounds the but-2-enyl anion reacts in conformity with the charge distribution to form an equilibrium mixture of butenes containing only ~3% of but-1-ene. [116,117,157] Hence migration of the reaction centre to the third carbon atom evidently occurs under the influence of the monomer. A similar effect is probable in the radical polymerisation of dienes, since the content of 1,2- and 3,4-units in the polymers considerably exceeds the equilibrium value and is independent of the temperature of polymerisation, whereas the ratio of *cis*- and *trans*-structures varies with temperature, approaching the equilibrium value. As noted above, formation of a carbon–metal σ-bond precedes entry of the monomer into the chain in coordination systems:



The formation of 1,2- and 3,4-units evidently corresponds to the case in which the α-form (B) is more advantageous than (A), which may be favoured by coordination of the transition metal with electron-donating solvating components, as in "cobalt" catalytic systems, and by the formation of π-complexes of vinyl groups with the transition metal



This provides an explanation for the preferential formation of syndiotactic units in the polymerisation of butadiene under the influence of various compounds of transition metals—cobalt, molybdenum, tungsten:



The complexes (A) and (B), formed alternately during chain growth, differ sterically in the position of the π-coordinating double bonds and the monomer. With π-allyl complexes of molybdenum crystalline syndiotactic 1,2-polybutadiene is formed [38-40]. It is noteworthy also that poly-π-allyl complexes of general formula π-R_nM usually cause predominant formation of 1,2-units, as has been shown for

$(\pi\text{-}C_3H_5)_4Cr$ [60,61], $(\pi\text{-}C_5H_9)_2Cr$ [29], $(\pi\text{-}C_4H_7)_3Ti$ [158], $(\pi\text{-}C_5H_9)_3Ti$ [24], $(\pi\text{-}C_3H_5)_3Nb$ [48].

An exception is π-R_3Rh, which is stereospecific for the production of *trans*-units [48].

III. CLEAVAGE OF CYCLOALKENES

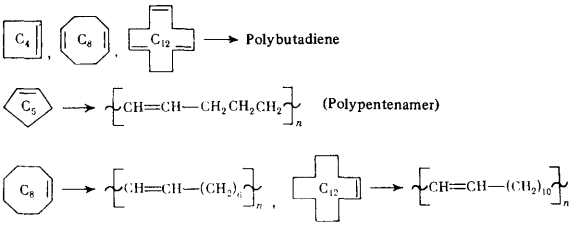
1. Mechanism of Dismutation

The cleavage of cycloalkenes is a novel route in coordination catalysis, revealing prospects for the synthesis of rubbers and other polymeric materials that cannot be obtained by the usual methods of polymerisation. The reaction was first described in Refs. 159 and 160. For some time the study of coordination catalysis developed in parallel and independently in the dismutation of alkenes and in the cleavage of cycloalkenes, until their completely identical nature was established with the possibility of initiation by the same systems. The catalysts used consisted mainly of organoaluminium compounds and halides of certain transition metals (tungsten, molybdenum, etc.). These catalytic systems (individual examples are given in Table 10) are closely similar in composition to Ziegler catalysts used for the stereospecific polymerisation of dienes and alkenes, but ineffective for the cleavage of cycloalkenes. An indispensable condition for Ziegler catalysis is formation of an organometallic compound in which chain growth takes place at the carbon–metal bond. It will be shown below that the cleavage of cycloalkenes and the dismutation of alkenes involve a new type of active centres.

Table 10. Systems used for the dismutation of alkenes and the cleavage of cycloalkenes.

Catalytic system	Ref.	Catalytic system	Ref.
$RAlCl_2+MoCl_3(NO)_2\cdot(PPh_3)_2$	161	$R_4Sn+WCl_6$	166
$RAlCl_2+WCl_2(NO_2)\cdot(PPh_3)_2$	161	$R_2Al+ReCl_5$	167
$RAlCl_2+WCl_6$	162, 163	$Mo(CO)_6+Al_2O_3$	168
$R_3Al(R_2AlCl)+WCl_6$	164	MoO_3/Al_2O_3	168
$R_3Al+MoCl_5$	164	Re_2O_7/Al_2O_3	169
$RLi+WCl_6$	165		

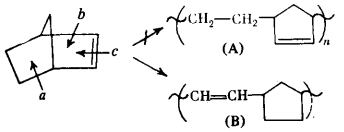
The polymerisation of cycloalkenes with homogeneous systems, which occurs very rapidly at low temperatures, yields products of high molecular weight that preserve the unsaturation of the initial cycloalkene:



The cleavage of cyclobutene, cyclo-octadiene, and cyclododecatriene yields polybutadiene. The possibility of obtaining *cis*-polybutadiene from cyclo-octadiene attracted the attention of research workers in connection with the

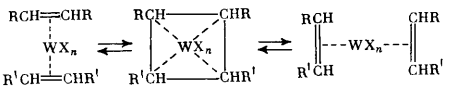
small heat of reaction (~8 kcal mole^{-1}). The fission of cyclopentene results in *cis*- and *trans*-polymers containing chains of five carbon atoms in the repeating unit and exhibiting rubberlike elasticity [170]. Depending on the ratio of *cis*- and *trans*-units either amorphous rubbers or crystalline *trans*-polymers melting at 73 and 83°C respectively are obtained from the cleavage of cyclo-octene and cyclododecene. The copolymerisation of different rings gives amorphous rubbers containing after completion of the reaction a random distribution of monomeric units in proportions corresponding to the composition of the initial mixture of monomers, independently of their relative reactivities. The reason is that the unsaturated polymer molecule also takes part in redistribution reactions [171-174].

It was supposed initially that cleavage of a cycloalkene results from rupture of a carbon–carbon bond adjacent to the double bond [175]. A study of the structure of polynorbornene.

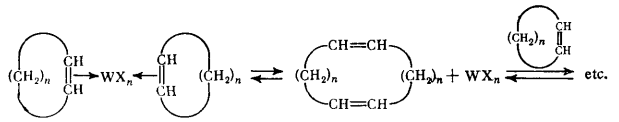


was adduced in support of such a mechanism. Cleavage of norbornene with rupture of a carbon–carbon bond in direction (*a*) should lead to formation of a polymer containing unsaturated five-membered rings (structure A). From the usual ideas on the nature of active centres of radical and ionic character it might have been assumed that this mode of rupture was the most advantageous, for the active centre would then be conjugated with the double bond. However, experimental data showed that the polymer had structure (B), which led to the conclusion [175] that the reaction followed path (*b*). It has since been established unambiguously [176,177] that ring cleavage takes place in direction (*c*): i.e. the polymerisation of cycloalkenes with ring fission is a particular case of the general reaction of alkene dismutation.

The mechanism suggested [178] for the dismutation of alkenes involved the formation of a "quasi-cyclobutane" intermediate complex of two alkene molecules in the coordination sphere of the transition metal:



This mechanism was transferred [179] to the polymerisation of cycloalkenes:



The above scheme entails a stepwise mechanism of polymerisation, in which dimers, trimers, etc. of comparable reactivity with the initial monomer (in the case of relatively unstrained rings) are formed successively. Hence in the initial stage of polymerisation the reaction system should comprise mainly oligomeric products of low molecular weight.

A chain process differs fundamentally from a stepwise process in the possible formation of products of high molecular weight even in the earliest stage of polymerisation, with a low yield of oligomeric forms. However, investigations of the polymerisation of various cycloalkenes have shown [173,174,180,181], that at the very start of the process—at degrees of conversion of 5–10%—polymers of very high molecular weight are formed (Table 11). The quantity of oligomeric products is small, and they are formed not by polymerisation but by cyclodegradation of polymers. Initial formation of products of high molecular weight is an indication of a chain mechanism and the appearance of extremely active centres effecting the chain process [173,174,182,183]. This conclusion must evidently be extended to the dismutation of alkenes. It is necessary to examine the individual stages of this process.

Table 11. Intrinsic viscosities of polymers obtained from cycloalkenes [173,177,180,181].

Cycloalkene	Catalytic system	Conversion, %	$[\eta]$, dl g^{-1}
Norbornene	$AlBr_3$—WCl_6—thiophen	13	5.5
	$(iso\text{-}Bu)_3Al$—WCl_6	11	2.4
	$(iso\text{-}Bu)_2AlCl$—WCl_6	9	1.8
Cyclopentene	$Si(C_6H_5)_4$—WCl_6	7.5	6.0
	$LiCH_2SiMe_3$—WCl_6	15	5.0
	$PhCHN_2$—WCl_4	10	7.8
Cyclo-octa-1,5-diene	$AlBr_3$—WCl_6—thiophen	12	2.3
	$(iso\text{-}Bu)_3Al$—WCl_6	11	1.5
	$(iso\text{-}Bu)_2AlCl$—WCl_6	12	0.9
	$PhCHN_2$—WCl_6	6	4.2
Cyclo-octene	$(iso\text{-}Bu)_2AlCl$—WCl_6	10	0.8
Cyclododecene	$(iso\text{-}Bu)_3AlCl$—WCl_6	5	0.7

Table 12. Polymerisation of cycloalkenes under the influence of carbene complexes (at 20°C).

Catalytic complex	Monomer (m)	$\frac{[m]}{[W]}$	$\frac{[RCHN_2]}{[W]}$	Duration of reaction, min	Yield of polymer, %	$[\eta]$, dl g^{-1}
$C_6H_5CH:WX_n$	cyclopentene	10^3	0.1	1	18.2	9
	cyclopentene	10^2	0.005	1	10	7.8
	cyclo-octa-1,5-diene	$5\cdot10^2$	0.01	1	6	4.2
$C_2H_5OCOCH:WX_n$	cyclopentene	10^3	1	15	65	0.77
	cyclopentene	10^3	0.2	20	62	0.82
	cyclo-octa-1,5-diene	$5\cdot10^3$	3	20	62	1.33

2. Initiation

All hitherto known active centres for chain polymerisation—free radicals, ions, ion-pairs, the usual coordination systems involving organometallic compounds—are ineffective for the cleavage of cycloalkenes and the dismutation of alkenes. We have undoubtedly met active centres of a novel type in the chain cleavage of cycloalkenes, which were regarded hypothetically [182,183] as complexes of carbenes with transition metals. An argument in support of their carbene nature was the formation of cyclopropane and methylcyclopropane when ethylene was kept over a dismutation catalyst [168]. Experimental results have been cited [180,184] that can be regarded as direct proof that monocarbene complexes are able to initiate the chain cleavage of cycloalkenes. The decomposition of phenyldiazomethane and ethyl diazoacetate in the presence of tungsten chlorides initiates the chain cleavage of cyclopentene and cyclo-octadiene with the formation of polymers of very high molecular weight. In the case of phenyldiazomethane the reaction occurs almost instantaneously at room temperature (Table 12).

The decomposition of diazo-compounds in the presence of salts of copper and certain other metals is a classical method for obtaining carbenes. The formation of products of very high molecular weight ($[\eta] = 4$–9 dl g^{-1}) indicates that the reaction involves very small quantities of long-lived active centres. Ordinary carbenes are extremely reactive in solution, adding non-selectively at C–H, C=C, etc. bonds. Their reactivity diminishes in the sequence

$$RCH{:},\ C_6H_5CH{:},\ (C_6H_5)_2C{:},\ ROC(=O)CH{:},\ (ROC)_2C{:}\ \text{etc.}$$

In several cases carbenes exhibit roughly the same selectivity on incorporation at tertiary, secondary, and primary carbon–hydrogen bonds [185] as do alkyl free radicals in abstracting the hydrogen atom.

Carbenes are stabilised to the greatest extent by coordination with transition metals. Thus many complexes of carbenes with zero- or uni-valent metals—chromium(0), molybdenum(0), tungsten(0), tellurium(0), manganese(I), rhenium(I), rhodium(I)—containing one or two oxygen, nitrogen, or sulphur atoms at the reaction centre $(RO)_2C:M$ are crystalline compounds stable at ordinary temperatures [186,187]. This indicates that coordination with a transition metal is energetically favourable to the formation of carbenes. The selectivity of carbene active centres towards the cleavage of cycloalkenes and the dismutation of alkenes is evidently connected primarily with their stabilisation on the transition metal.

The main types of redox systems involving transition metals and generating free radicals are well known:

$$\left.\begin{aligned} &ROOH + M^n \rightarrow M^{n+1} + RO^{\cdot} + OH^-\\ &ROOH + M^{n+1} \rightarrow M^n + RO_2^{\cdot} + H^+\\ &ROH + M^{n+1} \rightarrow M^n + RO^{\cdot} + H^+\\ &RH + M^{n+1} \rightarrow M^n + R^{\cdot} + H^+ \end{aligned}\right\} \quad (1)$$

$$A + M^{n+2} \rightarrow M^n + B: \quad (2)$$

The formation of free radicals (1) involves one-electron transitions in the course of oxidation or reduction of the metal. Reaction scheme (2) entails the possible formation of a carbene centre by the transfer of two electrons in a single step. Such a redox system, effective for the polymerisation of cycloalkene down to −70°C, has been studied [181,188] in the reactions of certain organolithium compounds—trimethylsilyl- and trimethylgermanyl-methyl-lithium—with tungsten hexachloride. The composition of the reaction products in benzene and $\alpha\alpha\alpha$-trideuterotoluene at 20°C is indicated [181,188] in Table 13. The appearance of trimethylsilyl and trimethylgermanyl chlorides is due to decomposition of an organotungsten compound accompanied by formation of a carbene complex:

$$(CH_3)_3Si\,(Ge)\,CH_2WCl_5 \rightarrow$$
$$(CH_3)_3Si\,(Ge)\,Cl + [CH_2 : WCl_4]\ .$$

The absence of deuteromethyltrimethylsilane on decomposition in $\alpha\alpha\alpha$-trideuterotoluene indicates that formation of this compound does not involve the trimethylsilylmethyl radical, which may result from homolytic breakdown of the organotungsten compound. Tetramethylsilane and tetramethylgermane may result [181,188] from disproportionation of two groups:

$$(CH_3)_3SiCH_2{-}WCl_4{-}CH_2Si(CH_3)_3 \rightarrow (CH_3)_4Si + [(CH_3)_3SiCH : WCl_4]\ .$$

This correlates with the increase in the yield of tetramethylgermane produced by raising the ratio of organolithium compound to tungsten(VI) chloride (Table 13).

The systems usually employed for the cleavage of cycloalkenes and the dismutation of alkenes—carbene active centres—can be formed in particular by isomerisation of the π-alkene complex:

$$\begin{matrix} RCH \\ \| \\ RCH \end{matrix} \rightarrow MX_n \longrightarrow \begin{matrix} RC:MX_n \\ | \\ RCH_2 \end{matrix}\ .$$

Such a scheme was suggested [189] to explain the formation of certain stable carbene complexes of platinum. Lower chlorides of tungsten (IV and V) by themselves initiate the polymerisation of cyclopentene when the catalyst is exposed to ultraviolet radiation [190]. The above mechanism for the generation of carbenes may operate in this case. In systems containing alkylating organic compounds of aluminium, tin, or other metals a carbene complex may be produced by the reaction

$$CH_3CH_2WCl_5 \rightarrow CH_3CH : WCl_4 + HCl \xrightarrow{R_3AlCl} RH + RAlCl_2\ .$$

This mode of decomposition can occur only in systems in which carbene formation becomes energetically advantageous as a consequence of stabilisation by coordination with a transition metal. Alkyl derivatives of many other transition metals—nickels, chromium, cobalt, etc.—break down [45,191,192] by a mechanism of disproportionation:

$$2RMX_n \rightarrow 2MX_n + R_{-H} + R_{+H}\ .$$

Table 13. Composition of reaction products.

RLi / WCl_6	Products isolated	Yield from RLi, mole %, in	
		C_6H_6	$C_6H_5CD_3$
1:1	$(CH_3)_3SiCl$	29—33	25
	$(CH_3)_4Si$	24—26	28
1:1	$(CH_3)_3GeCl$	44	—
	$(CH_3)_4Ge$	11	—
2:1	$(CH_3)_3GeCl$	34.5	—
	$(CH_3)_4Ge$	24.0	—

3. Mechanism of Chain Growth

A mechanism suggested [180,182,183] for chain growth under the influence of carbene complexes

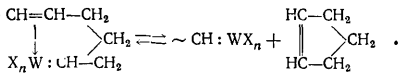
$$\sim CH : MX_n \longrightarrow \sim CH{=}CH{-}(CH_2)_n{-}CH : MX_n \longrightarrow \sim CH{=}CH{-}(CH_2)_n{-}CH{=}CH{-}(CH_2)_n{-}CH : MX_n, \text{ etc.}$$

involves the formation of linear polymer molecules. As the monomer concentration decreases, reaction of the carbene active centre with double bonds in the chain itself becomes more probable, leading to degradation and the formation of cyclic molecules:

$$\sim CH{=}CH{-}\underset{X_nM}{CH}{-}(p) \longrightarrow \sim CH : MX_n + \begin{matrix} CH \\ \| \\ CH \end{matrix}(p)\ .$$

In cases in which complex formation between the transition metal and the nearest double bond in the polymer chain is sterically highly probable, a polymer–monomer

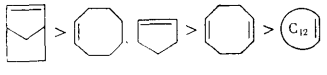
equilibrium is established, as has been found for cyclopentene [193]:



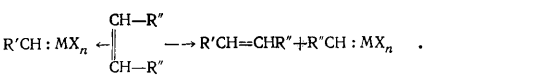
The position of equilibrium depends on the structure of the terminal unit. It lies closer to the monomer in the case of a *cis*-unit than with a *trans*-unit [194]. *cis*-Polypentenamer has been obtained under the influence of the system comprising tetra-allylsilane and tungsten hexachloride. With other cycloalkenes reaction of the active centre with a double bond in the actual chain yields a set of unstrained oligomeric cyclic molecules, the proportion of which increases with fall in the concentration of monomer and polymer in the solution. In dilute solutions linear polybutadiene of high molecular weight and polycyclo-octadiene undergo rapid cyclodegradation in the presence of above catalysts to form a set of cyclic oligomeric molecules (Table 14) [171,172,195]. In several systems equilibrium is established within 10–15 min, its position being determined by the polymer concentration in the solution. Cyclodegradation is characterised by the formation of oligomers having a very wide molecular-weight distribution ($\bar{M}_w/\bar{M}_n > 4$), which is consistent with results obtained by Stockmayer et al. [196] for ester polycondensation.

Catalytic system	Polymer	Polymer concn., wt.%	$\bar{M}_n$ of initial polymer	Time, min	$\bar{M}_n$ of polymer
WCl_6—$EtAlCl_2$	*cis*-polybutadiene	4	127 000	120	3 400
WCl_6—$EtAlCl_2$	*cis*-polybutadiene	8	220 000	25	9 000
$W(OR)_2Cl_4$—$EtAlCl_2$	*cis*-polybutadiene	8	220 000	30	1 000
$W(OR)_2Cl_4$—$EtAlCl_2$	polyoctadienamer	8	$[\eta] = 2.5$	30	0.20 dl g^{-1}

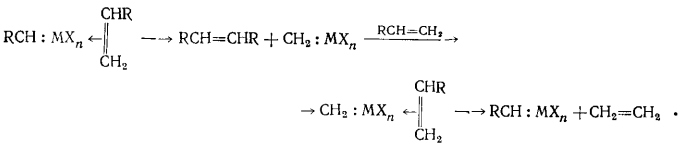
The general rules of the usual processes of radical or ionic copolymerisation are determined by the relative reactivities of the monomers and the corresponding active centres. No data are yet available that would enable us to estimate the relative reactivities of different carbenes coordinated with a transition metal. The nature of the active centres remains unchanged during the copolymerisation of unsubstituted cycloalkenes, since their entry into the chain is always accompanied by regeneration of the same type of active centre $\sim CH : MX_n$. According to their relative reactivities on copolymerisation r_1 and r_2 these compounds form the sequence [197–199]



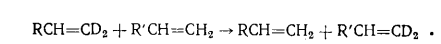
The dismutation of unbranched alk-2-enes, like the copolymerisation of cycloalkenes, involves carbene centres of the same type without thermal effects:



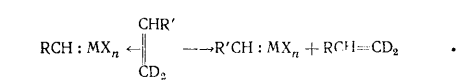
Under the influence of homogeneous catalytic systems this reaction is extremely rapid, as already noted. The dismutation of alk-1-enes in the same systems is very slow. The significance of this phenomenon is [188,200] that redistribution of alk-1-enes can take place only via alternating stages of transfer from secondary to primary carbene complexes:



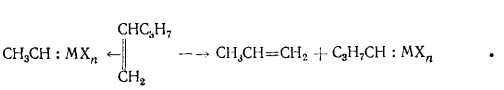
If the secondary carbene complex is rather less reactive than the primary complex, this should lead under conditions of a chain process to marked retardation of dismutation. Alk-1-enes are redistributed even more rapidly than are alk-2-enes with internal double bonds [201,202], but reaction is accompanied only by exchange of methylene groups:



Such a process occurs only with secondary carbene complexes:

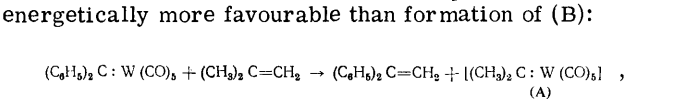


Experimental confirmation of the kinetic role of this factor has been obtained from investigation of the primary products of the codismutation of pent-1-ene and but-2-ene present in equimolecular proportions [203]. The homodismutation of pent-1-ene, involving alternating stages of primary and secondary active centres, should yield ethylene. Codismutation via secondary carbene centres seems more advantageous, and in the presence case should give propene:



The investigations [203] have shown that the chief primary reaction product is propene, with hardly any ethylene formed. When competing directions are possile, reaction occurs along the energetically most advantageous path.

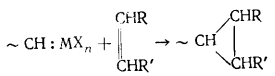
Interaction of the carbene complex $(CO)_5W : C(C_6H_5)_2$ with isobutene gives only 1,1-diphenylethylene, not 2-methyl-1,1-diphenylpropene. The reason can be understood on the basis that formation of the product (A) is energetically more favourable than formation of (B):



The complex (A) then decomposes to form propene. It has since been found [205] that, in the analogous reaction of the carbene complex $(CO)_5W : C(C_6H_4CH_3)_2$ with pent-1-ene, the yield of 1,1-ditolylethylene (and hence of the secondary carbene complex) exceeds 600-fold the yield of 1,1-ditolylpent-1-ene (and of the methylene complex B). It is important to note that diphenyl- and ditolyl-carbenes occupy a single coordination position on the tungsten atom, displacing one carbonyl group.

4. Possible Modes of Termination of Chain Dismutation

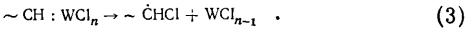
The problem of chain termination in dismutation must be considered in terms of the reactions of carbenes. The most specific reaction in solution is the formation of cyclopropane groups:



Such reactions occur also with coordinated carbenes. It has been shown[206] for various cyclopropane derivatives (n-pentyl, phenyl, n-butoxy) that under the influence of tungsten hexachloride and other components of catalytic systems they isomerise rapidly into the corresponding alkenes and conversion products of the latter. Thus the formation of cyclopropane groups results in chain termination. The appearance of linear alkenes during the polymerisation of cycloalkenes also lowers the molecular weight of the polyalkenamers, because such alkenes are involved in codismutation reactions.

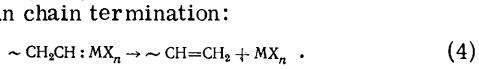
As in chain reactions of radical and ionic character, the cleavage of cycloalkenes and the dismutation of alkenes may be expected to be retarded or completely inhibited if the system is contaminated with alkenes capable of forming more stable carbene complexes. Possible examples of such compounds are alkyl vinyl ethers and 1,1-diphenylethylene, which are able to form centres of the type $ROCH:MX_n$ and $(C_6H_5)_2C:MX_n$. We have shown[184] that benzoylphenyldiazomethane, whose decomposition with the evolution of nitrogen is catalysed by tungsten(VI) chloride, does not initiate the polymerisation of cyclopentene.

Chain termination might occur also by reduction of the transition metal accompanied by formation of a free radical:



(3)

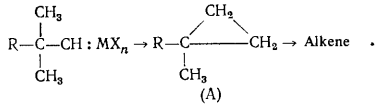
Migration of a hydrogen atom in the carbene complex will also result in chain termination:



(4)

The fundamental possibility of such a reaction has been demonstrated by Fisher[207] on alkyl-phenylcarbene–pentacarbonyltungsten model compounds.

The formation of polymers of very high molecular weight from cyclopentene in the presence of a diazocomponud and a tungsten halide[180] indicates that the role of reactions (3) and (4) is probably slight. But the probability of reaction (4) is increased by the presence of methyl substituents on the second carbon atom:



(A)

With the above secondary carbene in solution the yield of product (A) reaches 92–97%.[185]

The above ideas on possible ways in which a chain process initiated by a carbene complex can be terminated are based solely on analogies with the behaviour of carbenes in solution. Coordination with transition metals may change the picture significantly, and the specific reactions of such complexes have not yet been studied.

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