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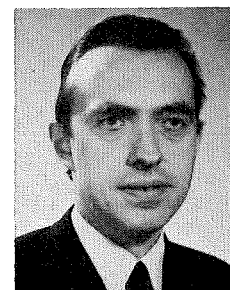
RECEIVED for review June 24, 1971
 ACCEPTED July 6, 1971

TECHNICAL REVIEW

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π -Allyl-Type Polymerization

Professeur A. LAFAYETTE

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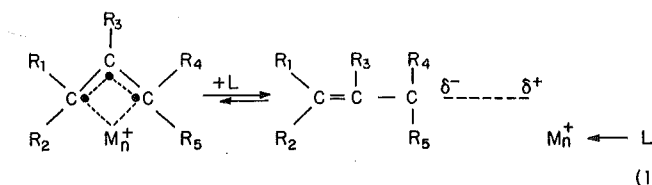
CHIMIE INDUSTRIELLE ORGANIQUE

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Many facts support the hypothesis that dienes react with a number of transition metal compounds to yield complexes of the so-called " π -allylic structure." Structural investigations of these complexes, especially by means of nmr spectroscopy, have shown that a metal ligand bond involves three carbon atoms, with the corresponding electrons being delocalized.



The π -allylic group may thus be considered as a bidentate ligand. If one end splits away from the metal atom, it is potentially replaceable by another ethylenic moiety; and the remaining end, now attached to the metal by a σ -bond, can act as an initiating center with some degree of anionic character.

Therefore, these compounds are of some interest as possible monometallic coordination catalysts in which the coordination site and the initiating center reside on the same metal atom.

Since the earlier discovery of π -allylic derivatives of transition metals by Fischer and Burger (1961), a great deal of research has been done on coordination catalysis initiated by π -allyl complexes concerning such reactions as the hydrogenation, isomerization, and oligomerization of conjugated diolefinic compounds.

Wilke and co-workers (1966) have in particular done a great deal of work on the synthesis and characterization of π -allylic complexes of transition metals, and they were successful in developing processes for the specific dimerization of propylene and the trimerization of 1,3-butadiene by π -allyl nickel catalysts. Many recent findings in the field of stereospecific polymerization indicate the formation of π -allylic type structures when conjugated dienes are polymerized with transition metal catalysts. The fundamental analogy between the 1,3-butadiene polymerization by some homogeneous Ziegler-Natta catalytic systems and that by some transition metal salts or π -complexes (i.e., alkyl, arene, cyclopentadienyl, carbonyl complexes) must be considered since all these classes of catalysts show a similar behavior and apparently proceed by means of the intermediary formation of π -allyl type complexes. Indeed, in these cases, the π -allylic bond is formed in situ by reaction between the diolefin monomer and the transition metal derivative. Reactions of this type are already well known in organometallic chemistry.

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π -allyl type polymerization is becoming increasingly important as many results in the field of the stereospecific polymerization reveal the general formation of π -allylic intermediates when conjugated dienes are polymerized by means of transition metal derivatives. The catalytic activity of simple π -allyl complexes of transition metals, as well as the structure of the polymers produced, are determined by the nature of the active center as a whole and are strongly influenced by both the transition metal itself and the ligands bound to the metal atom. In particular, the counter ion in the catalytic complex and some electron accepting or donating additives have been shown to control, with high precision and versatility, the overall reaction rate and the stereospecificity of the polymerization process. At the same time, the use of appropriate ligands yields a new type of stereoregular polydienes—e.g., the "equibinary" polymers. Kinetic data on π -allyl-type polymerization are briefly discussed, and tentative propagation is suggested to explain the significant experimental results now available.

Therefore, the catalytic activity does not necessarily depend on the existence of a preformed transition metal- π -allylic bond, since this bond can be generated by the action of the monomer, thus supporting the hypothesis that growth of polymer chains occurs by the insertion of the coordinated monomer on the π -allylic bond between the last polymerized unit and the transition metal.

Of great importance, therefore, are investigations on the stereospecific polymerization of conjugated diolefins by simple and pure π -allyl derivatives of transition metals, which can be considered as a good model (or at least a close precursor) of the active site structure.

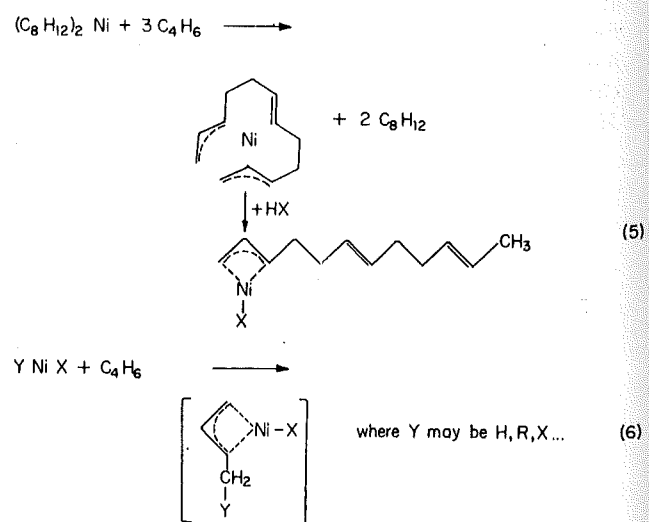
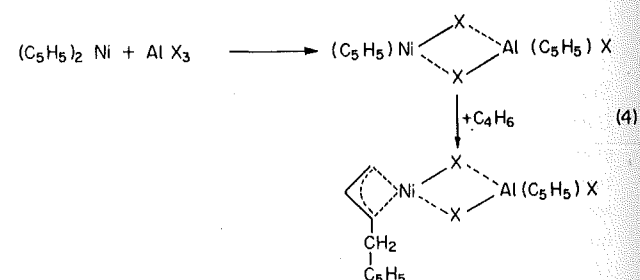
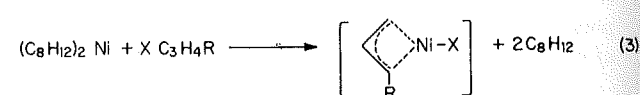
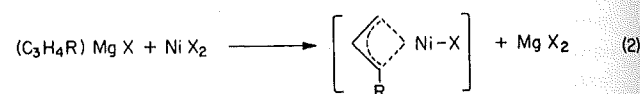
The first examples of stereospecific polymerization induced by simple π -allylic complexes of transition metals were reported separately by Porri (1964) and Wilke (1963). Wilke (1963, 1964) obtained a polybutadiene with a predominantly *cis*-1,4 content using $(\pi\text{-allyl})_2\text{Co(I)}$ as the catalyst and a high 1,2-polybutadiene with $(\pi\text{-allyl})_3\text{Cr}$. Porri et al. (1964, 1967) reported the butadiene polymerization by bis- $(\pi\text{-allyl nickel iodide})$ to crystalline *trans*-1,4-polymer and by bis- $(\pi\text{-allyl nickel chloride})$ in a benzene solution to predominantly *cis*-1,4-polymer. Since then, numerous studies have dealt with stereospecific polymerization with π -allylic derivatives of transition metals; but in spite of the large amount of work performed some of the data are still conflicting, and the proposed schemes for the mechanisms of diene polymerization with controlled chain growth are not yet fully satisfactory. Moreover, only a very few π -allyl type catalysts have been reported to achieve, without the need of any cocatalysts, the attractive performances of bimetallic catalytic systems (Ziegler-Natta type) regarding their activity as well as the properties of the polymers produced.

RESULTS AND DISCUSSION

Only a few π -allylic complexes of transition metals are able as such to promote the polymerization of unsaturated hydrocarbons, but most of them originally induce oligomerization reactions and become active polymerization catalysts only when $(\pi\text{-allyl} - M_T - X)$ species (X being any inorganic or organic counter anion) are generated, very often in situ, by the addition of various cocatalysts in the reaction medium.

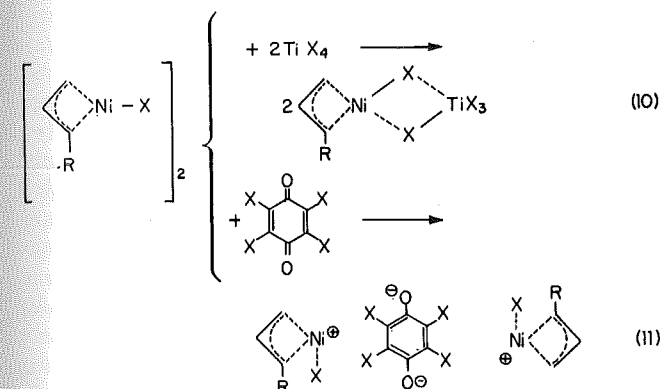
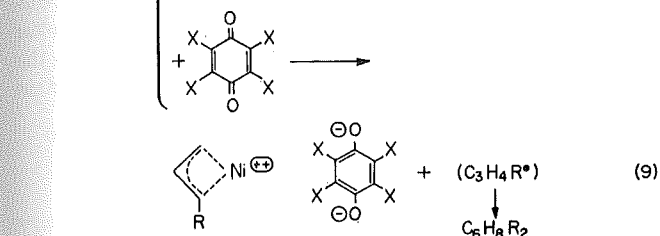
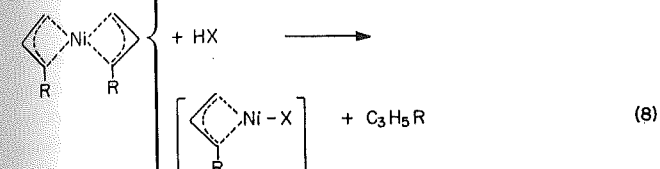
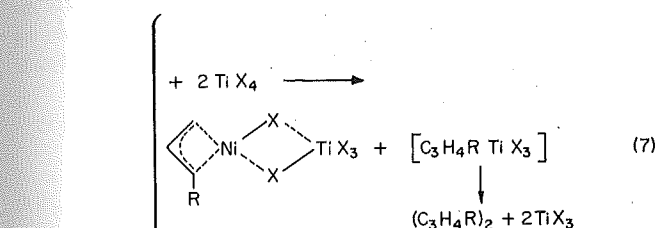
Synthesis of $(\pi\text{-Allyl } M\tau X)_m$ catalysts for the Polymerization of Unsaturated Hydrocarbons. Different reaction schemes can be used for the synthesis of anionic π -allyl complexes of transition metals. Such complexes can be produced by using suitable alkylating organometallic compounds to reduce transition metal derivatives (Reaction 2), and they can also be synthesized by oxidative addition reactions between reduced species of the transition metals with allylic derivatives (Reaction 3), metallic halides (Re-

action 4), and protonic acids (Reaction 5). Some of the reaction paths involve the interaction of the diene monomer as is also the case for the formation of π -allylic complexes directly from reduced salts or hydrides of transition metals (Reaction 6).



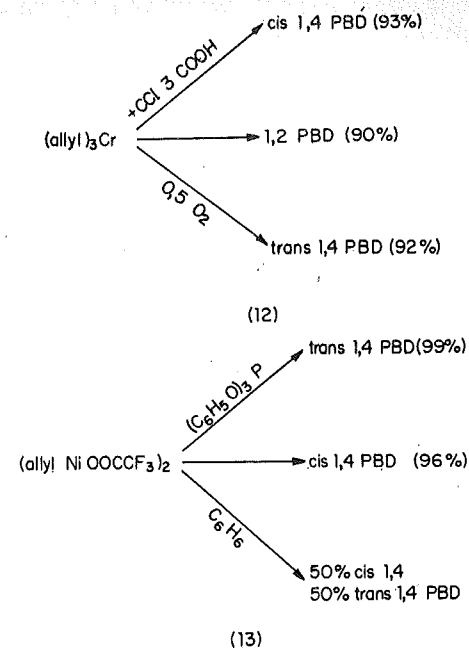
Moreover, inactive π -allylic complexes of transition metals may be transformed into active anionic species by reacting with metallic halides (Reaction 7), protonic acids (Reaction 8), or electron acceptors (Reaction 9) as cocatalysts, with some of the reactions further resulting in the formation of charge transfer complexes.

The enhanced catalytic activity of such complexes can also be obtained by adding metallic (Reaction 10) or organic (Reaction 11) electron acceptors to preformed halide or anionic π -allyl complexes.



Factors Influencing the Procedure of the Polymerization. Since the first step in polymerization on π -allylic complex catalysts is the formation of a π -complex of the monomer with the transition metal compound, many factors may have to be considered as influencing the procedure of the reaction. The structure of the polymers produced is determined, of course, not only by the transition metal itself but also by the nature of the active center as a whole influenced by the ligands bound to the metal atoms—i.e., the monomer, the counterion, and also the solvent and the nucleophilic or electrophilic additives eventually used. For example, by means of appropriate modifications of the catalytic species, it was possible not only to prepare the different isomeric structures of polybutadiene, starting from the same π -allylic transition metal (Reaction 12) (Oreskin et al., 1969), but also to synthesize three different isomeric compositions of 1,4-polybutadiene (Reaction 13) (Marechal et al. 1970).

Influence of the Transition Metal. Transition metal compounds with unfilled *d*-orbitals form complexes with unsaturated hydrocarbons active in the polymerization of olefinic



monomers. In this case, there is an overlapping of the filled π -orbitals of the olefin with the free d -orbitals of the metal coupled with the opposite effect of overlapping of the filled d -orbitals of the metal with the vacant antibonding orbitals of the olefin.

Depending upon which orbitals of the metal overlap with the π -orbitals of the olefin and upon the degree of overlapping of these orbitals and the atomic radius of the metals, complexes of the transition metals with monomers differing in their structure and consequently exhibiting different reactivities will be formed. On this basis, it should be expected that the structure and properties of the polymers formed will be determined basically by the nature of the transition metal.

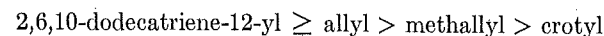
As summarized in Table I and as previously observed with Ziegler-Natta catalysts, the results obtained with π -allylic complexes confirm that the metals belonging to the right side of the transition series of the periodic system appear the most appropriate for the preparation of 1,4-polybutadienes (e.g., cobalt, nickel, iron, or rhodium), whereas metals from the center left yield predominantly 1,2-polybutadiene and promote the polymerization of monoolefins (e.g., chromium, molybdenum, niobium). However, the original specificity of some π -allyl complexes may be completely modified when anionic species are generated—i.e., the addition of hydrogen chloride to the chromium or niobium complexes results in the

Table I. Influence of Transition Metal on Microstructure of Polybutadienes Produces π -Allylic Catalysts

	Microstructure of polybutadiene		
Catalytic systems	% Cis- 1,4	% Trans- 1,4	% 1,2
$(\pi\text{-C}_4\text{H}_7)_2\text{Ni} + \text{NiCl}_2$	95	3	2
$(\pi\text{-C}_3\text{H}_5)_3\text{Co} + \text{I}_2$	90	2	8
$(\pi\text{-C}_4\text{H}_7)_3\text{Fe} + \text{FeCl}_3$	92	6	2
$(\pi\text{-C}_4\text{H}_7)_3\text{Rh}$	0	94	6
$[(\pi\text{-C}_4\text{H}_7)_2\text{Mo}]_2 + \text{MoCl}_5$	15	4	81
$(\pi\text{-C}_4\text{H}_7)_3\text{Cr}$	0	10	90
$(\pi\text{-C}_4\text{H}_7)_3\text{Nb}$	1	2	97
$(\pi\text{-C}_4\text{H}_7)_3\text{Cr} + \text{HCl}$	90	5	5
$(\pi\text{-C}_4\text{H}_7)_3\text{Nb} + \text{HCl}$	91	5	4

formation of *cis*-1,4-polybutadienes instead of vinylic polymers (Dolgoplosk et al., 1967).

Influence of the Structure of the π -Allylic Ligands Bound to the Transition Metals and of the Nature of the Monomers. Actually, only a few accurate data have been reported on the influence of the substitution of π -allylic ligands in halide catalysts (Medvedev, 1968), presumably on account of the relative stability and consequently the degree of purity of the tested complexes. However, in a homogeneous series of π -allylic nickel haloacetates, the overall rate constants for the polymerization of 1,3-butadiene appear to vary in the following order:



Furthermore, the influence of the π -allylic ligands bound to the transition metals must be related to the specificity of such catalysts toward the monomers which they polymerize as well as to the impossibility to get, with most of them, a true copolymerization, for example with butadiene. In fact, copolymers have been obtained from styrene with butadiene using π -allylic nickel derivatives as catalysts, but calculation of the monomer reactivity ratios indicates that butadiene is much more reactive than styrene.

Moreover, the intrinsic viscosity of the copolymer and the *cis*-1,4-butadiene content decreases sharply with an increase in the styrene content of the starting mixture (Ostrovskaya et

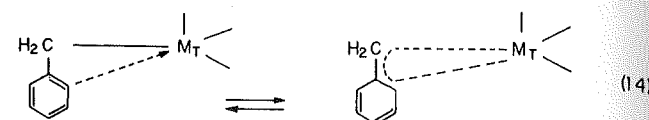
al., 1968). It is assumed that the bond formed by nickel with a styryl radical is less stable than the π -allylic bond formed by a butadiene molecule. The homopolymerization of styrene by π -allylic nickel complexes, leading to the formation of polymers having an average degree of polymerization of 8 to 10 (Matsumoto et al. 1968, Redkina et al. 1969) and some cases, specifically diphenylbutene-1, confirm this assumption.

Furthermore, as was observed a long time ago with Ziegler-Natta catalysts by adding suitable amounts of monoolefins to 1,3-butadiene, it is possible to control closely the mean molecular weight of the polybutadiene produced.

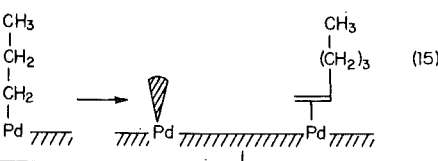
Indeed, insertion of the monoolefin yields a growing chain which must be bonded to the transition metal by a σ -type bond, and $\sigma\text{Co}-\text{C}$ or $\text{Ni}-\text{C}$ bonds are known to be very unstable at room temperature.

This also appears to be why the π -allyl nickel and cobalt complexes polymerize diolefins other than 1,3-butadiene, such as isoprene (Durand and Dawans 1970, Markevitch et al. 1969), 1,2-butadiene or allene (Nippon Gosei Gomu K. K. 1970, Otsuka and Kawakami 1965, Otsuka et al. 1965, 1967), but not α -olefins.

The polymerization of monoolefins is promoted in the presence of π -allyl chromium, zirconium, titanium, and molybdenum complexes; and partially crystalline polypropylene has been obtained by means of these complexes, with titanium tetrachloride or trichloride as cocatalysts (Farbwerke Hoechst A.G. 1966, Idemitsu Kosan Co. 1967, Imperial Chemical Industries Ltd 1969, Wilke 1964). It is not excluded that, in these cases, the polymerization takes place in fact on titanium catalytic species formed by the reaction of the cocatalysts with the π -allylic complexes. Moreover, some benzyl derivatives of titanium and zirconium have been reported to induce



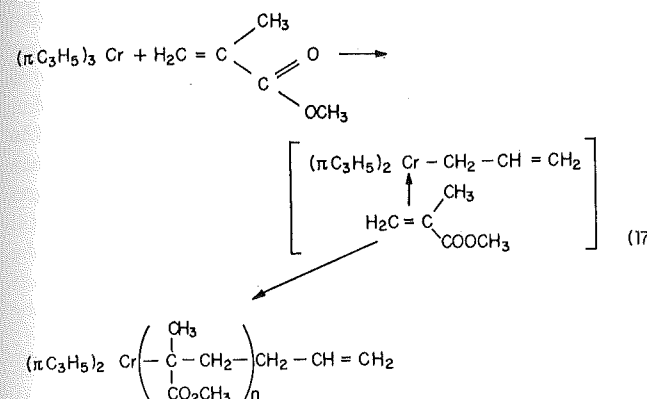
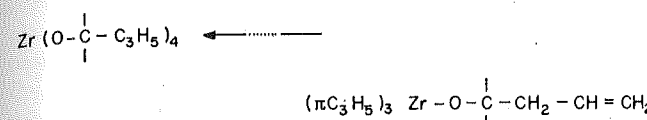
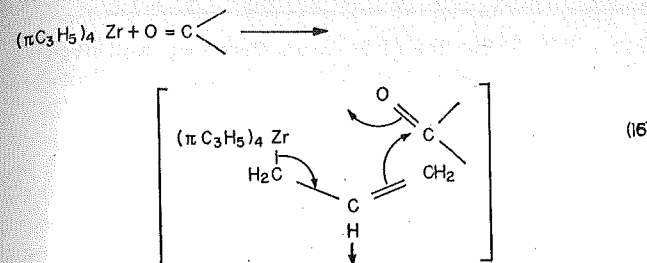
A peculiar π -allyl-type polymerization reaction (Ketley and Broatz, 1968) is the polymerization of propylene in the presence of palladium cyanide. This reaction yields a copolymer containing 93% ethylene and 7% propylene units. Since palladium cyanide is completely insoluble in the reaction medium, the reaction probably takes place at the crystal surface involving two adjacent palladium atoms, and the peculiar structure of the polymer produced is apparently due to the intermediary formation of a π -allyl type complex (Reaction 15):



A range of transition metal π -allyl compounds has been tested for the polymerization of vinyl polar monomers. They show considerable variation in activity, and not all vinyl monomers can be polymerized by these catalysts, although it appeared that monomers such as methyl methacrylate, acrylonitrile, and methacrylonitrile are polymerized by $(\text{allyl})_3\text{Cr}$ and $(\text{methallyl})_3\text{Cr}$ (Ballard et al. 1968). In fact, π -allylic complexes of transition metals can react with polar monomers in three distinct ways: Under suitable conditions, they can either polymerize the monomer, react with it to form a new organometallic compound, or form linear or cyclic oligomers.

The type of process which occurs is dependent on the nature of the allyl compound and the monomer. Compounds of the type $\text{Zr}(\text{allyl})_4$, $\text{Ti}(\text{allyl})_4$, and $\text{Mo}(\text{allyl})_4$ are inactive or inefficient as polymerization catalysts for vinyl monomers containing ester or carbonyl groups because of their marked tendency to form alkoxides (Reaction 16). Vinyl monomers containing nitrile group would also react to form metal-nitrile compounds rather than polymerizing. But addition of methyl methacrylate to π -allylic chromium complexes does not result in alkoxide compound formation (Reaction 17). It seems, that substitution of the α -hydrogen atom by a methyl group has inhibited association between the carbonyl group and the metal atom, which is a preliminary step for the formation of an alkoxide. In this particular system, therefore, polymerization is the preferred process and the tacticity of the polymethyl methacrylates obtained is slightly different from the one of the polymer produced by free radical initiation processes.

The polymerization of some cycloolefins has been performed in the presence of π -crotyl complexes of nickel, molybdenum, or tungsten and their reaction products with various Lewis



acids (Kormer et al. 1969). According to the reported data, these catalytic systems appear to be characterized by greater activity and stereospecificity than ordinary bimetallic catalytic systems. In fact, catalytic systems based on $(\pi\text{-C}_4\text{H}_7)_2\text{Ni}$ or $(\pi\text{-C}_4\text{H}_7\text{NiX})_2$ polymerize cyclobutene and cyclopentene exclusively at the double bond to yield the corresponding polycycloenamers. But opening of the rings is observed essentially in the presence of catalysts containing $[(\pi\text{-C}_4\text{H}_7)_2\text{Mo}]_2$ or $(\pi\text{-C}_4\text{H}_7)_4\text{W}$ resulting in the formation, respectively, of polybutadienes having 77 to 91% *cis*-1,4 and 23 to 9% *trans*-1,4 units or of polypentenamers containing 35 to 40% *cis* and 65 to 60% *trans* units.

Influence of the Counterion in the π -Allylic Complexes. The counterion used in the π -allylic complexes can influence both the stereospecificity and the overall activity, for example, in the process of 1,3-butadiene polymerization. Indeed, as shown in Table II, the microstructure of the polybutadiene produced by π -allyl complexes is a function of the nature of the anion in the complexes—i.e., chlorine complexes give a *cis*-1,4 configuration, whereas iodine complexes favor the formation of *trans*-1,4-polymers, and bromine complexes produce polymers of mixed *cis-trans* structure. The polymers obtained in all cases are essentially free from vinyl structure.

In fact, the decrease of *d*-electron density in the transition metal atom becomes more pronounced as the electron affinity of halogen increases. Thus, we can ascribe the relative high *cis*-1,4 contents of polybutadienes obtained with chloro catalysts to the low electron density of *d*-orbitals in the transition metal atoms as compared with that in bromo- or iodo-systems.

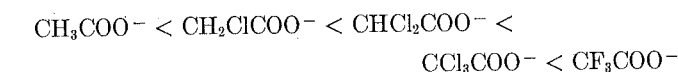
The *cis* content is still higher when a more electron withdrawing anion, such as a trihaloacetate, is used (Dawans and Teyssié, 1966). Even substitution in the counterion used can result in changes in the microstructure of the polymers obtained—i.e., high *cis*-1,4-polybutadiene is produced in the presence of π -allyl nickel picrate whereas the substituted bromide derivative yields a high *trans*-1,4-polymer (Yakovlev

Table II. Influence of Counterion in π -Allyl Nickel Derivatives on Microstructure of Polybutadienes Obtained

X^\ominus in $(\pi\text{-allyl NiX})_2$	Microstructure of	
	% <i>cis</i> -1,4	% <i>trans</i> -1,4
Cl	92	6
Br	72	25
I	2	96
OCOCF_3	97	2
$\text{OC}_6\text{H}_2(\text{NO}_2)_3$	94	4
$\text{OC}_6\text{H}_2\text{Br}_3$	0	96

et al., 1969a). In fact, the results obtained with different counterions seem to indicate that the change of stereospecificity is probably not due to a steric effect but mainly to the inductive effect of the counterion used.

Furthermore, the role of the counterion inductive effect in the π -allylic complex appears to be determinant in controlling not only the stereospecificity but also the overall rate of polymerization. Indeed, the substitution of the halogen in π -allyl derivatives of transition metals by anions from halogen-substituted carboxylic acids leads to a noticeable increase in the activity of the system (Durand et al. 1967, 1968). Moreover, the behavior of series of π -allyl nickel haloacetates, which are good catalysts for the *cis*-1,4-polymerization of butadiene, indicates an interesting correlation between the catalytic activity of the complexes and the electron-withdrawing properties of their coordinated counteranions (Dawans and Teyssié, 1969b). Their catalytic activities increase sharply in the following sequence:



with the overall polymerization rate with the trifluoroacetate ion being around 150 times as high as the one observed in the presence of a monochloroacetate counterion.

Moreover, very small amounts of the trifluoroacetate complexes—i.e., 100 ppm, are sufficient to initiate homogeneous *cis*-1,4 polymerization of butadiene and to produce a complete conversion within a few hours at room temperature. In addition to its catalytic properties, this π -allyl complex produces a *cis*-1,4-polybutadiene showing a similar set of characteristics to those of elastomeric polybutadiene samples obtained with Ziegler-Natta catalysts.

These data confirm the interesting possibility, by selecting the appropriate counterion, of isolating stable monometallic transition metal complexes which, without the addition of any cocatalyst, have similar catalytic properties to those of bimetallic systems.

Influence of Electron-Accepting Additives. Starting from π -allyl transition metal halides, enhanced catalytic activities may be achieved by adding various electron acceptors (e.g., metallic salts, iodine, derivatives of haloacetic acids and quinones as cocatalysts) (Dolgoplosk et al. 1968, Golenko et al. 1968, Lugli et al. 1969, Mushina et al. 1967, Yakovlev et al. 1969b).

In either case, the reaction leads to an increase in the effective charge on the transition metal atom (appearing as a result of bridging the halide anion in the charge transfer complex) and to an increase in its coordinating ability for monomers, and thereby an enhanced activity with respect to polymerization.

Table III. Influence of Electron-Accepting Additives on Microstructure of Polybutadienes Produced in Presence of π -Allyl Nickel Halides

Catalytic systems	Microstructure of polybutadiene	
	% <i>cis</i> -1,4	% <i>trans</i> -1,4
(π -Allyl NiX) ₂ + TiX ₄ (where X = Cl, Br, I)	88-91	4-8
(π -Allyl NiCl) ₂ + K ₂ SO ₄	90	8
+ MoCl ₆	91	6
+ AgNO ₃	92	5
+ Mg(ClO ₄) ₂	93	5
+ Ni(OCOCF ₃) ₂	95	2
(π -Allyl NiI) ₂ + SnI ₄	85	13
+ I ₂	84	15

As summarized in Table III, starting from π -allyl nickel chloride, most electron-acceptor salts used as additives have practically no effect on the microstructure of the polymer chain—i.e., a *cis*-1,4 structure is retained in all cases.

But starting from π -allyl nickel bromide or iodide, electron-accepting molecules not only accelerated the polymerization but also changed the stereospecificity, thus favoring *cis*-1,4 structure formation. In this case, it is quite obvious that the change in stereospecificity cannot be attributed to a halogen exchange reaction between catalyst components since catalytic systems containing only iodine [e.g., (C₄H₇NiI)₂ + SnI₄ or I₂] give predominantly *cis*-1,4-polybutadiene while the corresponding original π -allyl nickel iodide brings about the formation of a *trans*-1,4-polymer (Sharaev et al. 1967). Therefore, variation in catalytic activity and stereospecificity appears to be due to the formation of a charge transfer complex in which the electropositive charge on the transition metal atom is increased.

Such an increase in the positive charge on the metal atom can also be obtained by the action of organic electron acceptor molecules—i.e., the activity of the additive in π -crotyl nickel chloride increases as one goes from trichloroacetic acid to chloral and still further to trichloroacetic acid chloride and nickel trichloroacetate. This is indeed the direction of increasing the positive charge on the carbon atom of the carbonyl group—i.e., of its electron-accepting ability.

Similar observations were made depending on the type of substitution on quinones. The complexing ability of quinones, and consequently the stability of the resulting charge transfer complexes are all the higher as the half-wave potential for addition of the first electron is more positive. This potential, which is a measure of the electron affinity of the acceptor, is +0.01, -0.18, and -0.51 V, respectively, for *p*-chloranil, dichloro, or dibromo *p*-benzoquinone, and unsubstituted benzoquinone. Thus, in these series, *p*-chloranil has the highest complexing ability and *p*-benzoquinone the lowest, which is indeed in accord with their efficiency in increasing polymerization activity.

In the case of dichlorobenzoquinone, for example, a catalytically active complex formed only when starting from π -allylic nickel halides and not from bis(π -allyl)nickel. In the former case, less charge transfer is necessary because some has already occurred toward the halogen.

Finally, by use of highly electron-withdrawing counterions—i.e., trifluoroacetate—the overall rate of *cis*-1,4 polymerization, normally high, appeared not to be influenced by any of these additional electron-accepting compounds.

Table IV. Influence of Electron-Donating Additives on Microstructure of Polybutadienes Produced in Presence of π -Crotyl Nickel Chloride

Electron donors	Microstructure of polybutadiene	
	% <i>cis</i> -1,4	% <i>trans</i> -1,4
O ₂	88	10
(C ₂ H ₅) ₂ O	75	23
THF	54	41
C ₂ H ₅ OH	30	70
H ₂ O + KI	14	82
(C ₆ H ₅ O) ₃ P	4	93

Influence of Electron-Donating Additives. The introduction of electron-donor materials usually leads to a strong inhibition of π -allyl-type polymerization and to an increase in the amount of *trans*-1,4 (or even in a few cases of 1,2 units), as has been demonstrated with several Ziegler-Natta catalytic systems. In fact, when bases coordinate with transition metal ions, they donate an electron to the hydride σ orbitals of the metal ions, and at the same time, some parts of the resultant large negative charges on metal atoms are backdonated to the antibonding orbitals of bases to keep the metal atoms nearly neutral. Hence, the *d*-electron density of the metals is expected to be much more reduced, as the result of backdonation, as the basicity of the coordinated bases becomes larger. If, as is generally admitted, the nearly nonbonding *d*-orbitals play an important role in stabilizing the *cis* conformation of the butadiene to transition metal atoms, the *cis* content of polybutadiene should decrease when some bases (e.g., molecular oxygen, ethers, alcohols, water, phosphites) coordinate with the transition metal atom in the active species, as summarized in Table IV (Dolgoplosk et al. 1967, Matsumoto et al. 1969, Yakovlev et al. 1969b). The effects become more pronounced as the basicities increase and lead to a stabilization of the transition metal-carbon bond, resulting in a complete inhibition of polymerization, when the *d*-levels are filled by electron-donating compounds such as amines and phosphines.

Influence of Additional Ligands Yielding Specifically Equibinary Microstructures. A new kind of stereoregular polybutadiene, the equibinary poly (*cis*-1,4, *trans*-1,4) butadiene (i.e., a polymer containing equimolecular amounts of *cis*-1,4 and *trans*-1,4 isomers) has been prepared in our laboratory by modifying, with suitable additional ligands, π -allyl nickel complexes originally yielding *cis*-1,4-polybutadiene (Marechal et al. 1970, Teyssié et al. 1968). Depending on the nature of the additional ligand used—i.e., aromatic derivatives or trifluoroacetic acid—and on the ligand-to-nickel ratio, the *cis* and *trans* contents of the polymers produced are modified (while keeping a high 1,4 selectivity) until a 50/50 isomeric composition is reached. The equibinary stereospecific polymerization, not stated in the case of bimetallic catalytic systems, appeared to be a general phenomenon since equibinary poly(*cis*-1,4 -3,4)- and (-1,2 -3,4)isoprenes were obtained by modifying cobalt catalysts in a similar way (Dawans and Teyssié, 1967, 1969a).

In addition, an interesting peculiarity of the π -allylic catalysts promoting the formation of equibinary polybutadiene is the reversible character of the modification described—i.e., the addition of electron-accepting or -donating materials again promoting the formation of polymers having, respectively, an all *cis*-1,4 or crystalline *trans*-1,4 structure.

The observations made in the course of the study devoted to the catalytic species involved in the formation of equibinary poly(*cis-trans*)butadiene strongly suggest a competitive modification of the initial symmetry of the catalytic complexes by coordination of the additional ligands (Marechal et al. 1970). A tentative scheme of the formation of these equibinary polydienes has been proposed, occurring by alternate insertion of two different structural units in the chain through nonsymmetrical coordination positions on the catalytic complexes. Such a mechanism was further corroborated by the basic physical properties of the equibinary polydienes [i.e., the existence of a different crystallinity in the equibinary poly(*cis-trans*)butadiene from those observed in sequential poly-*cis*- or poly-*trans*-butadienes], due presumably to a regular alternate distribution of the isomers, at least in some sequences of the equibinary polymer chains.

Kinetic Data on Polymerization by π -Allylic Complexes of Transition Metals. The rates of polymerization of butadiene by various π -allylic complexes of transition metals are given by:

$$\frac{dM}{dt} = k(C)^{0.5}(M)^1$$

under the influence of bis(π -allylic nickel halides) (Harrod and Wallace 1969, Lazutkin et al. 1967, Medvedev 1968).

$$\frac{dM}{dt} = k(C)^1(M)^1$$

under the influence of bis(π -allylic nickel halides) and electron acceptors (Azizov et al. 1970, Pakuro et al. 1969, Vydrina et al. 1968, Yakovlev et al. 1969b) or of bis(π -allylic nickel trihaloacetates) (Marechal et al. 1970).

$$\frac{dM}{dt} = k(C)^2(M)^0$$

under the influence of tris(π -allylic chromium) (Oreskin et al. 1969).

In the case of bis(π -allyl nickel halides), the type of dependence of the overall rate of polymerization on catalyst concentration suggests that the active centers for chain growth are not the dimeric molecules of the original complex, but that the first step in the reaction is a dissociative equilibrium involving a monomer and determining the overall rate of the polymerization process. The total activation energy (ranging from 16 to 14.5 Kcal/mol) is surprisingly constant for all the bis(π -allyl nickel halides), independently of the nature of the halogen and the allyl group.

When electron acceptors are added to the catalysts, monomeric forms of the π -allylic complexes participate in the active center, and therefore the reaction order with respect to the catalyst concentration is equal to one. Depending on the electron acceptor used, the activation energy is decreased from 16 to 6 Kcal/mol.

Cryoscopic determinations have shown that π -allyl nickel trifluoroacetate is normally associated as a binuclear complex, but the addition of stoichiometric amounts of butadiene transforms the binuclear complex into a mononuclear species with a formation constant evaluated as 71 per mole. In this case, the polymerization rate was also found to be proportional to the first power of the nickel concentration, with the rate constant being 10 to 100 times as high as those measured with bis(π -allyl nickel halides); the total activation energy ranged from 10 to 13 Kcal/mol.

For butadiene polymerization by tris(π -allyl)chromium, the

second order found for the catalyst suggests that, in this case, the chain grows on a dimeric form of the complex in equilibrium with the mononuclear complex. Furthermore, it appears that the initiation process (formation of the catalytic species with monomer) is relatively fast, but the insertion of the monomer molecules into the chain would be rate determinant. Hence, the overall polymerization rate will be independent of the monomer concentration.

Mechanistic Data on the Stereospecific Polymerization of Butadiene by π -Allylic Complexes of Transition Metals. The stereoregularity of polybutadiene should be determined by the conformation that the butadiene molecule or the end of the growing polymeric chain assumes on coordination with the catalyst metal atom during the transition state of the polymerization reaction. Many reaction schemes and mechanisms have been envisaged, but they obviously do not represent a complete interpretation of the phenomena occurring in the stereospecific propagation, particularly for explaining the *cis-trans* orientation.

One of the most frequently proposed mechanisms (Kormer et al. 1969a,b; Dolgoplosk et al. 1968; Otsuka and Kawakami, 1965) is associated essentially with the structure of the growing chain end in the form of a π -allyl complex, with the "syn" form favoring *trans* polymerization and the "anti" form, *cis* polymerization, while the syn-anti orientation is eventually dependent on the coordination ability of the double bond nearest to the π -allylic polymer end. However, nmr data seem to exclude the coordination of the penultimate double bond and to suggest that only the "syn" form can exist as a stable complex in both substituted π -allyl nickel chloride and iodide, yielding, respectively, high *cis*-1,4 and high *trans*-1,4-polybutadienes (Durand et al. 1970, Frolov et al. 1967, Marechal et al. 1970, Matsumoto and Furukawa, 1967).

These observations suggest no correlation between the structure of the π -allylic ligand and the structure of the resulting polymer; of course, as an unstable transition state, a π -allyl complex with an "anti" form which undergoes polymerization prior to isomerization to the stable "syn" form is not necessarily ruled out.

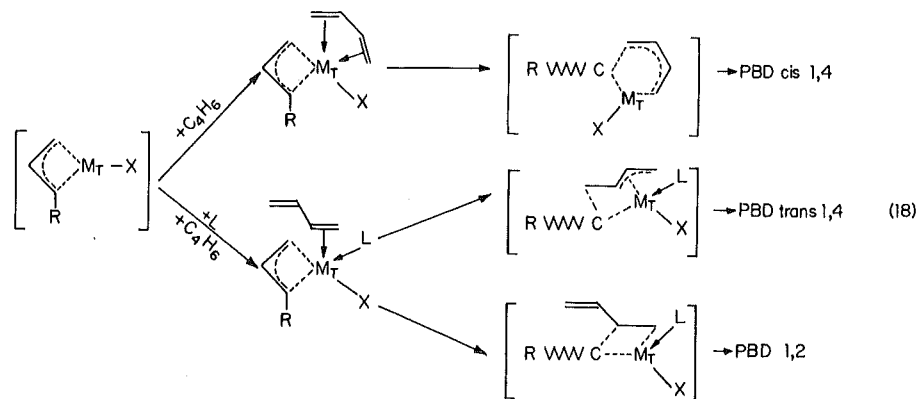
Another tentative interpretation of some of the facts observed was proposed on the basis of the dimeric or monomeric form of the complexes in solution (Dolgoplosk et al. 1970, Porri et al. 1967). However, at least in the case of nickel, the kinetic and cryometric data seem to exclude that a polymer chain can grow on a binuclear catalytic complex, and therefore it is difficult to explain the changes in the microstructure of the polymers produced solely on the basis of the monomeric or dimeric state of the catalysts.

Thus, the data currently available more and more support the concept that the polymerization proceeds through a σ -type transition complex whose structure is promoted prior to the addition reaction by the coordination of monomer with catalyst. This mechanism would not exclude the coordination of the growing chain to the metal by a π -allyl bond for most of the time, but it would assume that the allylic structure changes into an alkyl one under the influence of the coordinated monomer and prior to its insertion into the chain.

This mechanism also implies that the σ - π -isomerization does not modify the potentially *cis* structure of the last incorporated monomer unit, which is a point still open to debate. Then the process of the formation of *cis* and *trans* units will be determined essentially by the capacity of a transition metal to coordinate the diene molecule either by means of both its double bonds or by only one double bond. The formation of 1,2 units might take place when monomer coordination

involves one double bond and (1) if simultaneously the building of π -allylic complexes is impossible (in this case, polymerization would proceed entirely via σ -bond formation), or (2) if the atomic distances favor the 1,2 joining.

If we take into account all the experimental information now available, the mechanism of the formation of stereoregular polybutadiene in the presence of π -allylic complexes can tentatively be summarized as follows:



The propagation of the chain would proceed by the repetition of basic reactions including the formation of a π -complex between the catalyst and the diene, eventual isomerization of the π -allyl (if any) to a σ -complex, and reaction of the σ metal-alkyl bond with the coordinated monomer to give the same complex as initially, with further coordination of another butadiene molecule.

Within the framework of this mechanism involving six- to four-membered transition states, the structure of the initial complex between the catalyst and the diene determines the microstructure of the polymer chain (nevertheless a reaction mechanism, implying either that the growing chain end remains constantly σ -bonded to the metal atom during the propagation or that the π -allylic group subsequently formed after each insertion step keeps an "anti" configuration in the transition state, would more readily account for the cis or trans orientation of the 1,4 isomers). In this scheme, the action of electron-donating additives which are capable of competing with the bidentate diene for a site in the coordination sphere of the catalyst becomes understandable. Only a monodentate complex may be formed under these conditions, and this leads to the *trans*-1,4-polymer. If the tendency toward complex formation is greater, the added substance can begin to compete with the π -allyl group responsible for the occurrence of 1,4 addition, and then 1,2-polybutadiene is formed.

CONCLUSIONS

π -allylic derivatives of transition metals are usually well defined and relatively stable monometallic catalysts for the polymerization of various monomers.

More particularly, they are very efficient catalysts for the stereospecific polymerization of 1,3-butadiene with some of them even showing the same activity and specificity as the best Ziegler-Natta systems.

It proved possible to obtain stereoregular polybutadienes with different microstructures according to the nature of the ligands bound to the transition metal, and a new type of stereospecific polymerization yielding equibinary polydienes was revealed by modifying π -allyl complexes.

Such elaborate control of the stereospecificity by means of monometallic catalytic species should encourage the development of π -allyl-type polymerization for the production

of stereoregular polymers or even copolymers having modified properties, starting from conventional monomers.

Simultaneously, all the experimental observations already obtained in the field of π -allyl type polymerization led to a more detailed picture of the catalytic centers involved in the stereoregulation processes.

However, much more experimental work is obviously needed to clarify these concepts, and anyway it is felt that the

determination of the geometry of the active species by means of concerted physical methods (i.e., combined esr, nmr, magnetic susceptibility and spectrophotometry) performed directly on the reaction solutions would help the understanding of the mechanisms of these coordinated reactions.

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RECEIVED for review July 10, 1970
 ACCEPTED April 12, 1971

Lecture presented at the Joint CIC/ACS Conferences, 159th Meeting, Toronto, Canada, May 24-29, 1970.