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OLIGOMERIZATION CATALYSTS
V. BIS(CYCLOOCTATETRAENE)IRON(0): SYNTHESIS, CONVERSION TO OTHER COMPLEX COMPOUNDS, AND OLIGOMERIZATION MECHANISM

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SUMMARY

The synthesis and reactions of bis(cyclooctatetraene)iron(0) are described. An interpretation is offered of the mechanism of the oligo- and cooligomerization of different unsaturated hydrocarbons promoted by iron complexes.

INTRODUCTION

Some oligomerization reactions of unsaturated hydrocarbons catalyzed by organometallic iron compounds have already been reported[1-4]. In particular, the catalytic behaviour of bis(cyclooctatetraene)iron(0) (I) was described and compared with that of some two-component catalyst systems, prepared from trivalent iron salts and organometallic compounds. The catalytic reactivity of (I) was related to its unique structure, which involves a new type of intra- and inter-nuclear valence tautomerism[2]. We here describe the chemical reactions of (I), and propose a mechanism for the oligomerizations promoted by iron complexes.

PREPARATION AND CONVERSION REACTIONS OF BIS(CYCLOOCTATETRAENE)IRON(0)

We obtained (I) by reaction of an ethereal isopropyl Grignard solution with ferric chloride in the presence of cyclooctatetraene:

$$FeCl_3 \xrightarrow[C_8H_8]{(iso\text{-}C_3H_7)MgCl} \underset{(I)}{Fe(C_8H_8)_2}$$

Isopropyliron probably forms as an intermediate (cf. ref. 5), but its reductive de-alkylation to bis(cyclooctatetraene)iron occurs without UV irradiation. This reaction is complete at $-30°$ within a few hours.

(I) is not very stable in the reaction medium but is indefinitely stable at room temperature in the crystalline state or in diethyl ether or hydrocarbon solutions, provided that oxidizing agents are absent. It is fairly soluble in chlorinated hydrocarbons, but the solutions are quite unstable, and ferrous chloride rapidly precipitates.

As previously mentioned[1], a benzene solution of (I) reacts with carbon monoxide to yield the known cyclooctatetraene tricarbonyliron complex, with release of one mole of cyclooctatetraene.

Treatment of a toluene solution of (I) with one or two moles of bipyridine gives a black precipitate and the supernatant solution becomes dark green. Based on the IR spectrum and conversion products, we attribute to the black powder the formula $C_{20}H_{16}FeN_4$ and the structure of bis(bipyridine)iron(0) (II). Such a compound has been recently reported[6], but little is known of its properties*. The IR spectrum of (II) shows characteristic absorption bands at 1568, 1286, 1269, 1013, and 969 cm^{-1}. Some of them are very close in position to those of free bipyridine, the small shift probably being due to coordination. Solutions of (II) in polar aprotic solvents are paramagnetic. When an aqueous solution is taken to dryness, the material obtained shows a UV maximum at 518 nm, attributed[7] to the ion $[(Bipy)_3Fe]^{2+}$.

An excess of bipyridine converts (I) to the known $(Bipy)_3Fe^0$ complex[8].

(I) reacts with terpyridine in petroleum ether at 0° to give a black-violet solid of empirical formula $C_{30}H_{24}FeN_6$. The violet compound recovered from an aqueous solution of this solid contains the ion $[(Terpy)_2Fe]^{2+}$ (UV maximum at 552 nm[9]).

As previously mentioned[3], (I) reacts with diphenylacetylene (tolane). From reaction in toluene at 30–40° or diethyl ether at 0°, we isolated two crystalline complexes of iron. The complex formed in toluene contains clathrated toluene and therefore differs from that prepared in ether. The elemental analysis indicates the presence of five tolane units per iron, three of which, as shown by the NMR spectrum, are certainly bound as hexaphenylbenzene; it is still not known whether the remaining two are coordinated to iron as such or as a dimer, *e.g.* as tetraphenylcyclobutadiene or as a five-membered iron-containing ring. Thermal and oxidative decompositions (induced by halogenating agents, like $FeCl_3$, $HCl+O_2$) of both complexes yield hexaphenylbenzene and tolane. The structure of these complexes will be described after completion of the X-ray analysis.

(I) does not react in solution under moderate conditions with N_2, H_2, allyl chloride, or triphenylphosphine.

Carbonylation of (I) does not modify the oxidation state of iron, but (I) is oxidized by proton acids or Lewis acids. Anhydrous HCl at −78° decolourizes the brown ether or toluene solutions of (I) with precipitation of light-coloured, fairly unstable products, in which the metal partially exhibits an ionic character. The absence of free cyclooctatetraene in solution suggests that the iron, even in the oxidized state, still binds cyclooctatetraene or its protonated species. This is also consistent with the strong reactivity of these products versus air and with their solubility in solvents

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* Bis(bipyridine)iron(0), (II), as prepared by us, is highly reactive: it takes up even traces of oxygen, to give a red, water-soluble compound; in oxygen it inflames spontaneously. In hydrocarbon suspension it absorbs one mole of oxygen, releasing part of the bipyridine. It is thermally unstable and is gradually converted into a brown product with loss of bipyridine. It is substantially insoluble in hydrocarbons, but dissolves in polar solvents, such as dimethyl sulfoxide, alcohols, or water, yielding red solutions, from which it cannot be recovered unaltered. It shows a weak catalytic activity in the oligomerization of unsaturated hydrocarbons. When suspended in liquid butadiene at 50°, it is slightly soluble and yields a violet solution which dimerizes butadiene in low yield (< 20%) to a ~2.5/1 mixture of 1,5-cyclooctadiene and 4-vinylcyclohexene. If ethylene is present in addition to butadiene, small amounts of *cis*-1,4-hexadiene are formed. (II) is also catalytically active in the hydrogenation of ethylene to ethane, a reaction which easily takes place at 50° and 10 atm.

like methylene chloride.

Boron trichloride resembles proton acids in the oxidation of iron in both ether and hydrocarbon solutions; unstable, boron-containing products with saline character are formed.

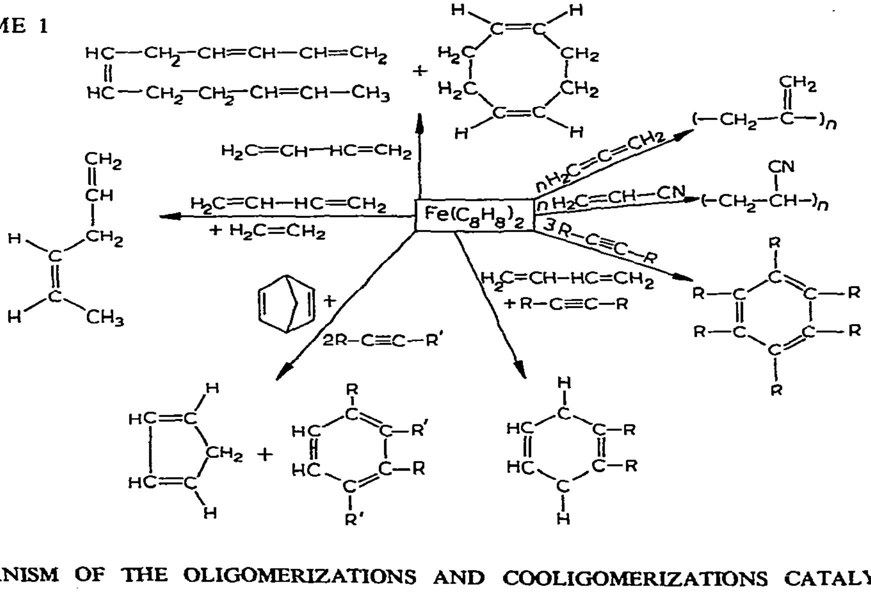
CATALYTIC ACTIVITY OF BIS(CYCLOOCTATETRAENE)IRON

(I) promotes several selective oligomerizations and cooligomerizations of unsaturated hydrocarbons[1-4]. Monomers suitable for such reactions are: conjugated dienes, such as butadiene, isoprene, or pentadiene; certain non-conjugated dienes, such as norbornadiene; mono-olefins, such as ethylene and propylene; mono- and disubstituted acetylene; and, according to our recent findings, also cumulated olefins, like di- and tetrasubstituted allenes[10]. (I) does not catalyze the polymerizations of α-olefins and conjugated dienes, but it induces rapid polymerization of allene and acrylonitrile to known polymers.

Both the oligomers and cooligomers obtained in these reactions are nearly exclusively dimers or trimers. Some of them are open-chain unsaturated hydrocarbons, whereas the others are cyclic olefins or benzene derivatives. In some cases, open-chain and cyclic olefins are formed simultaneously.

Scheme 1 illustrates the most significant reactions among those catalyzed by (I):

SCHEME 1



MECHANISM OF THE OLIGOMERIZATIONS AND COOLIGOMERIZATIONS CATALYZED BY BIS(CYCLOOCTATETRAENE)IRON

The catalytic behaviour of bis(cyclooctatetraene)iron is peculiar in that other coordination complexes of zerovalent iron* are completely unable to promote the above reactions. The reactions are however, promoted by two-component iron

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* *e.g.* monocyclooctatetraene tricarbonyliron, monocyclohexadienemonobenzeneiron.

catalysts of the Ziegler–Natta type, namely by those prepared from trivalent iron (chloride, acetylacetonate) and organometallic compounds of aluminum[11,3,4], magnesium[12], or alkaline metals[13,14], both in the presence and in the absence of phosphorus-containing ligands[15,16]. Because of its broad spectrum of catalytic activity in the oligomerization of unsaturated hydrocarbons and its well-defined structure[1,2], (I) appeared to us particularly suitable as a model compound for the study of the mechanism of the oligomerizations promoted by iron-containing catalysts*.

Oligomerizations induced by these catalysts may be subdivided into two classes:

(1) those in which cyclic oligomers are formed and where the formulation of the reaction mechanism does not require migration of hydrogen[17];

(2) those in which a migration of hydrogen from one to another of the complexed molecules is involved, with consequent formation of open-chain oligomers.

The reactions of the first type are formally self-explanatory, whereas those of the second class may not be immediately visualized. For example, four different dienes: *cis*-1,4-hexadiene, *trans*-1,3-hexadiene, 1,5-hexadiene and 3-methyl-1,4-pentadiene may be obtained in the ethylene–butadiene codimerization. 1,3-Hexadiene is formed by hydrogen migration from butadiene to ethylene, the other three isomers by hydrogen migration from ethylene to butadiene. In the latter case, a 1,4-addition yields 1,4-hexadiene, and a 1,2-addition 1,5-hexadiene or 3-methyl-1,4-pentadiene depending on whether the ethylenic hydrogen migrates to the internal or to the terminal carbon atom of butadiene, respectively.

The hydrogen involved in migration always stems from an external methylene group, attached to the molecular skeleton by a C=C double bond. This important characteristic of these oligomerizations is experimentally supported[18].

When a solution of (I) in liquid butadiene is kept for some hours at 0°, the cyclooctatetraene originally bound to iron is released (as indicated by the NMR spectrum) while butadiene oligomers are simultaneously formed. During the whole reaction the solution remains completely homogeneous and hence the iron is present in a soluble species. This means that:

(1) oligomerization takes place in the homogeneous phase;

(2) butadiene displaces cyclooctatetraene, at least in part, from coordination sites around the iron[2];

(3) the actual catalytic agent arises from a zerovalent iron, to which the olefins to be oligomerized are complexed;

(4) the catalytic agent does not contain halogen atoms.

The zerovalent iron complexes probably have a trigonal bipyramidal structure with five coordination sites, as suggested by the tendency of Fe^0 to assume a noble gas configuration accepting ten electrons from the donating ligands (in this case the olefins)[19].

Butadiene and the other olefin monomers are presumably π-bonded to the iron, like cyclooctatetraene in the starting complex (I). Butadiene may be complexed

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* The above analogy actually suggests that also in the Ziegler–Natta iron oligomerization catalysts the real catalytic agent arises from an olefin complex of zerovalent iron and that the role of the organometallic compound is merely that of reducing the trivalent iron. Our considerations on $Fe(C_8H_8)_2$ should therefore be applicable also to the Ziegler–Natta iron catalyzed oligomerizations.

through two double bonds, occupying two coordination sites, or through one double bond, occupying only one coordination site. Actually, butadiene complexes of zerovalent iron have been described, in which the butadiene molecule is bonded to the metal through two π-bonds, in a *cisoid* conformation (*e.g.* in butadiene tricarbonyliron[20,21]), or through one π bond, in a *transoid* conformation (*e.g.* in butadiene tetracarbonyliron or in butadiene octacarbonyldiiron[22]).

The type of diene complexation (1,2 or 1,4; axial or equatorial), and hence the particular iron–olefin complex formed, depends on the relative basicity of the olefins (including cyclooctatetraene), and on the presence of ligands and on their relative concentrations*.

The second major problem is concerned with the question of which type of bond is active in the oligomerizations. We consider now only the formation of open-chain oligomers originating in hydrogen transfer reactions. The two types of mechanisms, most frequently involved in coordination catalysis, are considered:

(1) insertion into a pre-existing metal–carbon or metal–hydride bond;
(2) oxidative addition followed by reductive elimination.

In the first type of mechanism the bonds most frequently involved are:

(*a*) σ-alkyl(or hydride)–iron bonds;
(*b*) σ- or π-allyl–iron bonds.

These bonds may originate in alkylation of the iron compound by the metal alkyl or in the addition of the first unsaturated unit to an iron–hydride bond formed by the reaction of the catalyst components as suggested by Iwamoto and Yuguchi[16].

Any insertion mechanism into a pre-existing bond presupposes an inter-oligomeric course of the reaction, inasmuch as the hydrogen or the alkyl group forming the active bond arises from an oligomer formed previously to the oligomer molecule to be considered. The oxidative addition mechanism, on the contrary, allows a formulation of the oligomerization without involving a hydrogen or alkyl carrier from outside the complexed molecules that form a given oligomer molecule.

(1) *Insertion mechanisms*

A σ-alkyl–transition metal bond is generally postulated in the Ziegler–Natta polymerization of α-olefins. In our case such bonds could not be found in $Fe(C_8H_8)_2$, and their formation during the reaction with butadiene or ethylene appears unlikely. Firstly, it is well known that σ-alkyl–iron bonds are very unstable unless strong stabilizing ligands are present[23]. [In the bis(bipyridine)diethyliron complex the σ-ethyl–iron bond is stabilized by the bipyridine groups, but it catalyzes the oligomerization of butadiene only after the ethyl groups are split off thermally[6]]. Second, one should find alkyl end groups in the oligomers. Third, when carbon monoxide is bubbled in a butadiene solution of (I) at 0°, replacement of the cyclooctatetraene ligands by butadiene occurs, but no organic carbonyl compounds are formed. Different behaviour is found with nickel catalysts[24].

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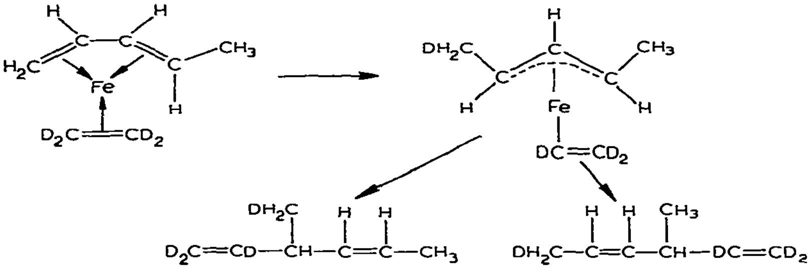
* No proved correlations exist between the type of coordination and the structure of the addition products or between the characteristics of the present oligomerizations and the polymerizations of olefins and diolefins promoted by analogous Ziegler–Natta catalysts. However, we have found that catalysts prepared from iron salts and trialkylaluminum convert a butadiene/ethylene mixture to oligomers along with small amounts of polybutadiene built up from 1,4 and 1,2 units, whereas an analogous catalyst complexed with $P(C_4H_9)_3$ yields pure 1,2-polybutadiene.

The presence of an active π-crotyl–iron bond[16] is inconsistent with the following experiment. (I) was allowed to react with liquid butadiene at −30° until the NMR spectrum indicated the displacement of all, or at least the major part, of the cyclooctatetraene ligands by butadiene. Thereupon all the unreacted butadiene was removed, and the remaining complex was treated with methanol. The products contained butadiene and no butenes. On the other hand when this complex was treated with anhydrous hydrogen chloride in diethyl ether, essentially 1-butene was formed. Finally, when the complex was treated first with methanol and then with hydrochloric acid, only butadiene was recovered. These results indicate that active π-crotyl–iron bonds are not present in an appreciable amount, and that the recovered butadiene was complexed to iron. The absence of hydrogen in the products from treatment with methanol or hydrogen chloride suggest the probable absence of a stable metal hydride intermediate.

We also must take into account an experimental finding reported recently[25]. A complex of zerovalent iron, $Fe(Ph_2PCH_2CH_2PPh_2)_2 \cdot CH_2{=}CH_2$, in the absence of organometallic compounds, codimerizes butadiene and ethylene to yield, among other products, 1,5-hexadiene, the only linear hexadiene free from methyl groups. Since the isomerization of any hexadiene always leads to conjugated dienes, 1,5-hexadiene is obviously a primary reaction product and must be formed by a migration of hydrogen from ethylene to an internal butadiene carbon atom in a 1,2-type addition. The presence of σ-alkyl–iron or π-crotyl–iron bonds is not consistent with this result, because these bonds would give rise, by insertion reactions, to dimers or codimers containing methyl end groups.

An allyl mechanism can not explain the simultaneous formation of *cis*-1,4-hexadiene and *trans*-1,3-hexadiene in the butadiene/ethylene codimerization. Actually, whereas the formation of the first is not incompatible with a π-crotyl–iron intermediate, since it would require a migration of hydrogen from ethylene to butadiene, the second codimer would have to be formed by hydrogen migration from butadiene to ethylene, whereas butadiene must receive and not lose a hydrogen in order to give a π-crotyl residue.

In addition to the evidences reported above, which are in disagreement with an allyl insertion mechanism, we have carried out a further crucial test. By codimerizing *trans*-1,3-pentadiene with perdeuterated ethylene in presence of the tris(acetylacetonato)iron/$AlEt_3$ catalyst system[26] we obtained a 3-methyl-*cis*-1,4-hexadiene consisting exclusively of isomer (IV) instead of an equimolecular mixture of isomers (III) and (IV), as required for an allyl mechanism by the symmetric structure of a hypothetic π-allyl intermediate complex:



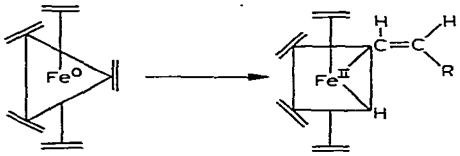
Isomer(III) Isomer(IV)

This means that the complexed pentadiene molecule that is converted to methylhexadiene does not enter a symmetric π-allyl transition state and reacts only by 1,4-addition.

For the above reasons we can exclude the two insertion mechanisms.

(2) *Oxidative addition mechanism*

Oxidative addition followed by reductive elimination seems the most likely mechanism. The first of these steps is often proposed for the catalyses promoted by transition metals, especially those of the VIIIth Group[30]. Starting from five-coordinated trigonal bipyramidal complexes of zerovalent iron, oxidative addition implies a hydrogen abstraction from the external carbon atom of a vinyl group of one of the coordinated monomers. This monomer may be either an ethylene or a butadiene molecule. The question of which monomer undergoes the hydrogen abstraction can be answered by considering the stereochemistry of the complex. It has been shown[27] in the case of the butadiene dimerization induced by $CoC_{12}H_{19}$ that the hydrogen closest to the metal is the one that can be abstracted. The complex should thus assume an octahedral configuration with six coordination sites around a formally bivalent iron, as illustrated in the following scheme:



Octahedral coordination complexes of bivalent iron are known[23]. The formation of an octahedral intermediate should, we consider, be favoured by the electron acceptor capacity of the σ-bonded vinyl group. Hydrogen is probably also σ-bonded to the iron. No direct evidences for the proposed intermediate has yet been found but none of the experimental findings are in disagreement with our hypothesis.

As to the further reaction step, *i.e.* the reductive elimination of the two σ bonds with formation of the oligomer, analogous cases are described in the literature[28]. It could involve the simultaneous rupture of the two bonds and the addition of hydrogen and vinyl or butadienyl residue to a coordinated second monomer; depending on the conformation of this molecule this may be a 1,2 or a 1,4 addition*. The proposed mechanism requires the reformation of a zerovalent iron, to which the oligomer remains complexed until it is displaced by new incoming monomers.

This mechanism may be strictly applied only to formation of open-chain oligomers, but can be reformulated to account for the formation of cyclic oligomers. For conformational reasons, it is possible that no hydrogen atom is sufficiently close to the metal to undergo abstraction. Oxidation of the iron catalyst is not necessary to explain the formation of cyclic oligomers, but the existence of a transition state involving a five-membered cyclic intermediate containing two σ iron–carbon bonds cannot be excluded.

In conclusion, we think it reasonable to attribute the formation of the various cyclic and open-chain oligomers essentially to geometrical characteristics of the in-

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* The proposal of simultaneous addition to a butadiene unit coordinated in *cisoid* conformation is in agreement with the formation of the pure *cis* isomer of 1,4-hexadiene.

termediate coordination complexes. We think that the simultaneous formation of different oligomers from the same monomer with a single zerovalent iron catalyst can be explained by assuming that different coordination complexes between the olefins and iron are simultaneously formed, and that these are in equilibrium among themselves and differ in the number and in the geometrical disposition assumed by the olefins, especially the butadiene molecules, in their coordination around the iron.

The simultaneous formation of four different hexadienes (*cis*-1,4-hexadiene, *trans*-1,3-hexadiene, 1,5-hexadiene, 3-methyl-1,4-pentadiene)[31] may thus be easily explained by the different complexation of the butadiene molecules to the iron. The first one may result from a dicoordinated butadiene, whereas the remaining three hexadienes may stem from monocoordinated butadienes. The difference between the last two depends on whether the hydrogen migrates from the vinylic butadiene to ethylene or *vice versa*, which difference should be governed by the stereochemistry of the complex and depend on which methylenic hydrogen is the closest to the iron.

EXPERIMENTAL PART

Reagents

Anhydrous $FeCl_3$ was sublimed before use. Cyclooctatetraene and bipyridine were commercial products. Butadiene (Phillips special purity) was distilled and dried over molecular sieves.

The solvents (toluene, pentane, diethyl ether) were commercial products dried with $LiAlH_4$ and distilled under nitrogen atmosphere. Ethylene-d_4 was prepared according to the literature[29] in an isotopic purity of 98%.

Preparation of bis(cyclooctatetraene)iron

All operations were carried out under anhydrous nitrogen atmosphere. $FeCl_3$ (1.5 g) was dissolved in diethyl ether (50 ml) in a 100 ml three-necked glass flask, equipped with mechanical stirrer and connected with a dropping funnel. After addition of cyclooctatetraene (6.5 ml), the solution was cooled to $-45°$, and a 2.8 *M* solution of (iso-C_3H_7)MgCl in diethyl ether (14 ml) was added with stirring from the dropping funnel during 20–30 min. The suspension formed was stirred at $-30°$ for about 8 h, then cooled to $-78°$ and filtered. Ether was removed by evaporation at a reduced pressure (0.1 mm) at $-30°$. The solid residue was thoroughly dried and extracted with successive amounts (80–100 ml) of anhydrous n-pentane cooled to $0/-30°$. The dark brown pentane solution was cooled to $-78°$ to give black crystals, which were recrystallized from n-pentane to give about 0.5 g of long shiny black needles. n-Heptane and toluene/n-heptane may also be used for the recrystallization.

Reaction of (I) with bipyridine

(I) (0.2 g) was dissolved in toluene (10 ml) at 0°. Bipyridine (0.12 g) in toluene was added, and the mixture was kept overnight at 0°. During that time its colour changed from brown to green-black and a black solid was deposited. This was filtered off, washed with toluene and n-pentane, and dried. (Found: C, 64.66; H, 4.57; Fe, 14.98; N, 14.78. $C_{20}H_{16}FeN_4$ calcd.: C, 65.23; H, 4.35; Fe, 15.20; N, 15.22%.)

Protolysis of the catalytic complex

(I) (75 mg) was dissolved in liquid butadiene (2 ml). The solution was maintained at 0° for 3 h. Gas-chromatographic analysis showed the presence of 1,3,6,10-dodecatetraene and 1,5-cyclooctadiene. The solution cooled to $-30°$ was dried under reduced pressure, and the residue was treated three times with cold n-pentane, then dried, kept at $-30°$ at 0.001 mm for 1 h and then treated with a solution of methanol in n-pentane. The resulting solution was shown by GLC analysis to contain butadiene (about 7 mg); butenes were absent. The gaseous phase was free from hydrogen. In a similar experiment the residue was treated with anhydrous HCl in diethyl ether: GLC showed 1-butene to be essentially the sole volatile product.

Codimerization of 1,3-*pentadiene–ethylene-*d_4

The reaction was carried out under the conditions used for the ethylene/1,3-pentadiene codimerization[26]. The reaction products were separated by preparative GLC (column 6 m long, ∅ 1 cm, Carbowax 1500, 20% on Chromosorb, programmed 70–120°, 10 °/min, 1 kg/cm^2 He). The position of the deuterium atoms of 3-methyl-1,4-hexadiene (purity >99%) were determined by NMR analysis (Varian HA, 100 Mc, room temperature, TMS standard). The spectrum showed signals at τ 8.44 (m, 2, DCH_2) and 9.0 ppm (d, 3, CH_3).

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