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Homogeneous Transition-Metal Catalysis in Asymmetric C–C-Bond Formation. Back to Coordination Polymerization

Giambattista Consiglio*

Abstract. An account is given of the development of the author's research in the field of homogeneous catalysis by transition-metal complexes at the Laboratorium für Technische Chemie of the ETH, Zürich. The main goal is to explore the potentiality of asymmetric transition-metal catalysis for new reactions in which C–C bonds are formed, leading to enantiomerically enriched (pure) products. Increasing attention is given to new carbonylation reactions, in particular to their exploitation for the synthesis of new stereoregular optically active polymers.

Introduction

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Homogeneous Transition-Metal Catalysis in Asymmetric C–C-Bond Formation. Back to Coordination Polymerization

Giambattista Consiglio*

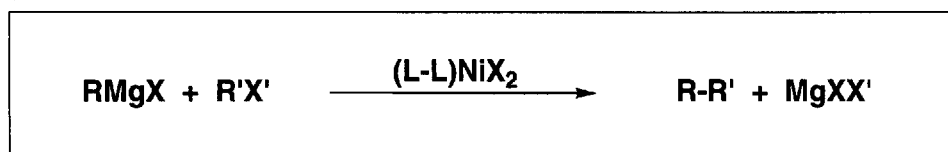
Abstract. An account is given of the development of the author's research in the field of homogeneous catalysis by transition-metal complexes at the Laboratorium für Technische Chemie of the ETH, Zürich. The main goal is to explore the potentiality of asymmetric transition-metal catalysis for new reactions in which C–C bonds are formed, leading to enantiomerically enriched (pure) products. Increasing attention is given to new carbonylation reactions, in particular to their exploitation for the synthesis of new stereoregular optically active polymers.

Introduction

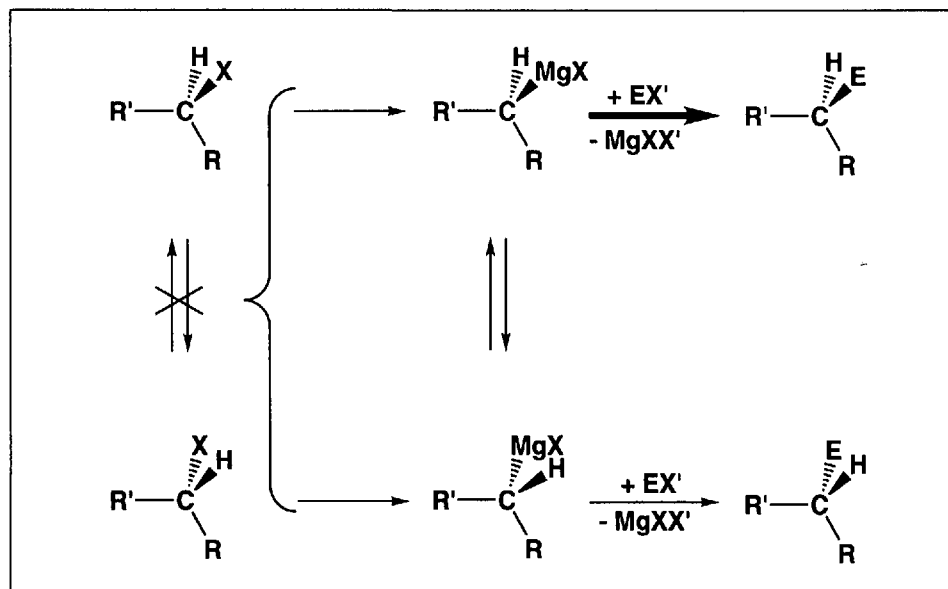
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Scheme 1



Scheme 2



Ziegler-Natta catalysts. The approach I chose was to attempt to exchange hydrocarbon residues between boron [1] and compounds of the other elements [2]. I was unsuccessful, but I learned that secondary C-atoms, bound to metals such as magnesium or aluminium, normally racemize rapidly [3][4].

After completing my service in the army, I joined the group of the late Prof. P. Pino at the ETH-Zürich, in September 1968. Again I conducted research in the field of *Ziegler-Natta* catalysis, in particular trying to synthesize soluble catalysts. This meant at that time the synthesis of organometallic compounds of titanium- and aluminium-containing organic groups lacking β -H-atoms [5]. Those systems revealed low activity and almost no stereochemical control in the polymerization of α -olefins [6][7]. This research developed slowly and without promising results, and I began to look for other research topics. Switching from diastereoselective *Ziegler-Natta* catalysis to enantioselective catalysis was a small conceptual step for two reasons: *i*) the basic ideas were similar [8] and *ii*) the development of asymmetric catalysis by transition-metal complexes had begun to produce spectacular results in hydrogenation [9], particularly as a consequence of the introduction of chelate ligands [10]. Hydroformylation catalysis was then in a crucial phase due to the

introduction of rhodium phosphine complexes [11]. I had begun to acquire some knowledge of that reaction [12]. Since, from the very beginning, we had some difficulty in reproducing the synthesis of the chiral diphosphine 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane [10], we tried to purify it by complex formation and decided to prepare a nickel complex [13].

Kinetic Resolution of *Grignard* Reagents

During the first half of 1972 I was impressed by two papers related to cross-coupling using nickel complexes as the catalysts [14][15] (*Scheme 1*); in fact, the reaction scheme represents conceptually the easiest way to form C-C bonds. In particular examples were given in which alkyl *Grignard* reagents were used to couple [15]. Remembering the facile racemization of chiral *Grignard* reagents in which the metal is bound to the asymmetric C-atom, and since we had a chiral nickel complex at our disposal, the possibility of achieving the first asymmetric cross-coupling reaction was soon considered. In fact, starting with chiral, racemic halides, the asymmetric cross-coupling reaction (*Scheme 2*) offers, in principle, the possibility of transforming a chiral, racemic compound completely in a single enantio-

mer. We submitted the first examples of such a reaction using halogenated hydrocarbons as the electrophilic reagents for publication in *Helv. Chim. Acta* at the end of 1972 [16].

Homogeneous catalysis by transition-metal complexes was not very popular in Switzerland at that time, in spite of the excellent work being carried out by the group of the late Prof. H. Schmid at the University of Zürich [17]. Therefore, I suppose that no one interested in catalysis read the paper, whose results were published again by Japanese colleagues almost one year later [18]. This disappointed me but eventually led to a sincere friendship with the group of Prof. M. Kumada in Kyoto.

The asymmetric cross-coupling reaction has become a popular reaction among those catalyzed by transition-metal complexes [19]. About twenty different groups have published in the field. M. Kumada, T. Hayashi and coworkers [19] developed amino phosphines based on ferrocene or derived from amino acids and reached very high enantioselectivities. Their basic idea was to introduce in the catalytic species a basic group able to interact with the *Grignard* reagent and to prepare it for the asymmetric reaction.

We were mostly interested in understanding the reasons for enantioselectivity. In fact, asymmetric induction in the reaction could be determined during the formation of the transition-metal alkyl intermediate or be the result of a kinetic resolution of that intermediate and of its epimerization at the asymmetric C-atom. This alternative is suggested by the fact that the coupling reaction is normally accompanied by a coupling co-product which arises from a formal isomerization of the hydrocarbon residue from secondary to primary and by reduction products of the electrophilic reagent. In fact, it appears difficult to conceive an experiment to determine the stereochemical aspects of the reaction.

One of the problems we faced during our investigations was related to the reproducibility of the results. With time, we discovered that this effect was due to the activation of magnesium with iodine prior to the preparation of the reagent. The magnesium diiodide thus formed can interact with the *Grignard* reagent, giving rise to mixed species which are believed to give the transition-metal *sec*-hydrocarbon-residue intermediates with an enantioselectivity different to that observed in the absence of the magnesium halide [20]. Based on this observation we suspect that the transalkylation reaction of the transi-

tion-metal compound by the *Grignard* reagent is indeed stereospecific [21][22] and, therefore, determines the stereochemical outcome of the coupling reaction.

Since the coupling reaction is accompanied by the formation of magnesium salts we expected on the basis of the aforementioned influence of magnesium iodide, that the enantioselectivity might depend upon the extent of conversion. We tested the validity of our hypothesis in the coupling reaction of 1-phenylethylmagnesium bromide with vinyl chloride using nickel-dibromide complexes containing *trans*-cyclopentane-1,2-diylbis(diarylphosphine) as the chiral ligand and we found that this is indeed the case [23]. Only for the ligand (*S*)-(*Rp*)-1-[1-(dimethylamino)ethyl]-1',2-bis(diphenylphosphino)ferrocene (which had been developed by colleagues in Japan [19]), we found no effect of the conversion, thus supporting the original idea that the amino substituent could 'prepare' the *Grignard* reagent to give an univocal species responsible for the transalkylation reaction.

Asymmetric Alkylation of Allylic Electrophiles

Kinetic resolution of the *Grignard* reagents also takes place using allylic electrophiles [24]. In this case, however, the centre of chirality can also derive from the allylic substrate, which can be either prochiral or chiral [25]. Starting with chiral allyl alcohols we determined the overall *anti*-stereochemistry of the reaction at the level of the allylic moiety [26]. This was the first example of alkylation taking place with net inversion of configuration using VIII group metal complexes. The complementarity with the net retention observed with similar systems using more soft nucleophiles should be appreciated [27].

The determination of the stereochemistry of the reaction helped us to define the structure of the possible reaction intermediate (*Fig. 1*). We envisaged the possibility of achieving high asymmetric induction in the reaction by using C_2 ligands in order to reduce the number of possible intermediates. The ligand and the two reaction partners must all be on the metal, thus allowing the total exploitation of the steric requirements of the ligand during migration of the R substituent on either terminus of the allyl moiety. This was indeed the case, and high enantioselectivity was achieved. However, we could recognize that there is an optimum size of the alkylating group for high enantiomeric

excess to be achieved [28]. Smaller groups do not allow us to completely use the stereochemical constraint of the ligand, whereas larger groups probably cause a change in the mechanism to be operative.

Enantioselective Carbonylation Reaction

a) Low Molecular Weight Compounds

The carbonylation reaction of olefinic substrates allows easy entry into oxygenated compounds such as aldehydes or esters (*Scheme 3*, [i] and [ii]) and has been the subject of investigation for many years.

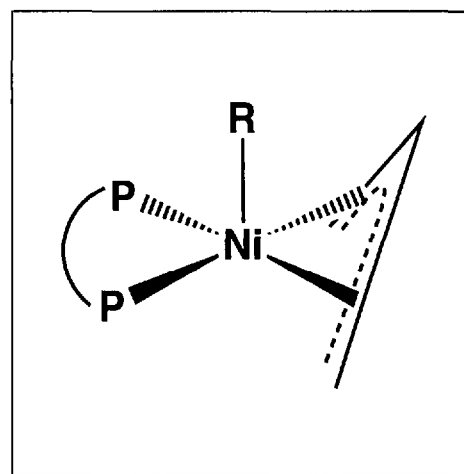
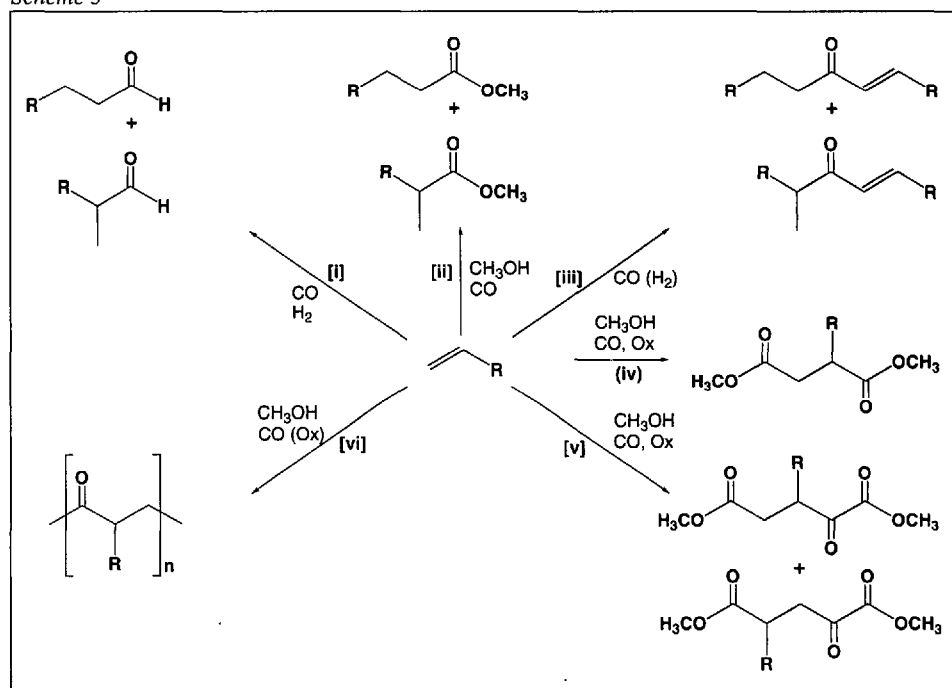
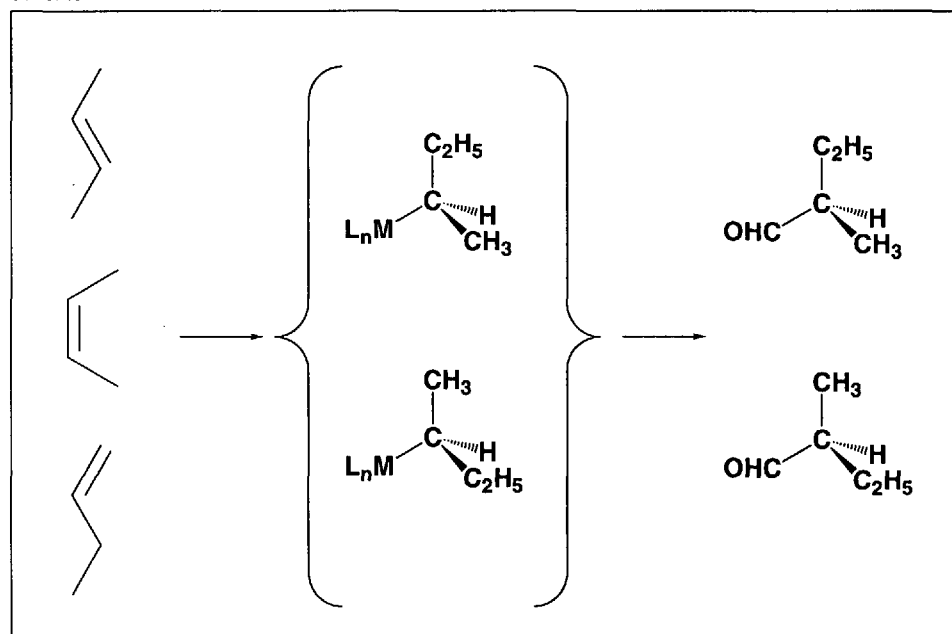


Fig. 1. Possible reaction intermediate

Scheme 3



Scheme 4



Only recently has the reaction been used to produce compounds derived from more than one molecule of olefin and/or CO. In particular, it seemed of value to investigate hydroformylation (*Scheme 3*, [i]), because of the large variety of possible substrates [29]. The results, as far as enantioselectivity is concerned, were disappointing because of the low optical yields. Nevertheless, we obtained important information for the field of asymmetric catalysis by transition-metal complexes, namely about the step of the catalytic cycle in which asymmetric induction is determined. We looked for substrates having different structures, such as the linear isomeric butenes, but which would give the same reaction intermediate, the *sec*-butyl transition-metal derivatives (*Scheme 4*).

For all catalytic systems, without exception, investigated to date, the enantiomeric composition of the aldehyde products does reflect the differences between the starting substrates, thus inferring the optical stability of the *sec*-alkyl metal intermediate. The stereochemical stability of such intermediates was further demonstrated by the determination of the clean

syn-addition to the C=C bond during the reaction [29]. We assume, therefore, that the stereochemical outcome of the reaction is determined before or during the formation of the alkyl complex. For the related hydro-alkoxycarbonylation reaction (*Scheme 3*, [ii]) it seems [30] that enantioface selection during the irreversible (or at least not completely reversible) formation of the olefin π -complex intermediate could be reflected in the enantioselectivity of the reaction. It is noteworthy that, in this case, enantiomeric excesses in the formation of the isomeric aldehydes will be influenced by the regioselectivity of the process [29]. In any event, the outcome of the reaction does, in some way, reflect the relative energy of the competitive four transition states leading to the alkyl complex (*Fig. 2*, X = H).

In spite of the interest in synthesis for asymmetric hydroformylation and of the activity of various research groups in this field, enantioselectivity remained rather low when phosphine-rhodium complexes were used as the catalyst precursor. The introduction of the less chemoselective platinum catalysts and of 'phosphole' (=

9*H*-9-phosphafluorene) ligands caused a great improvement in the enantioselectivity, at least for aromatic olefins [31].

Our understanding of the low enantioselectivity in hydroformylation by rhodium was based on the interpretation of the effect of H₂ and CO partial pressure on enantioselectivity [29]. We assumed the existence of different catalytic species that display different enantioselectivities. This assumption recently received some support by other research groups which recognized two ways of coordinating chelate ligands in a pentacoordinated trigonal bipyramidal rhodium intermediate, namely diequatorial and equatorial-axial [32][33]. Diequatorial coordination seems to be more effective for asymmetric hydroformylation [32]. Recent developments, which were based more or less implicitly on this approach, have led to a considerably improvement in the enantioselectivity of the rhodium-catalyzed hydroformylation [34][35].

The analogous synthesis of esters through hydro-alkoxycarbonylation (*Scheme 3*, [ii]) using palladium catalysts precursors of the type L₂PdCl₂ was even less successful, probably due to the low catalytic activity of those systems [29].

During attempts to prepare more active catalytic systems based on palladium complexes containing anions, which are relatively easily displaced in a second coordination sphere [36][37], we discovered the possibility of an asymmetric synthesis of 2-substituted butanedioates (*Scheme 3*, [iv]). This was the first enantioselective synthesis of succinic-acid derivatives via the 'double' carbonylation reaction of an olefin [38]. We were, therefore, interested in finding conditions under which the selectivity of the reaction would be improved. We did indeed find those conditions, but we also found that, at high CO partial pressure, a synthesis of 3- or 4-substituted 2-oxopentanedioates takes place (*Scheme 3*, [v]) even if with low chemoselectivity (up to ~30%). The latter reaction represented a still unknown 'triple' carbonylation of olefinic substrates [39] which takes place with rather high enantioselectivities, the enantiomeric excess being higher than 91% for styrene. The fact that the products of the double and triple carbonylation of styrene, namely dimethyl 2-phenylbutanedioate and dimethyl 2-oxo-3-phenylpentanedioate, show the same optical purity suggests that they are formed through the same reaction intermediate or transition states, namely the one arising from a secondary insertion of the styrene substrate (*Fig. 2*, X = COOR', a and b). Secondary insertion of styrene into a pal-

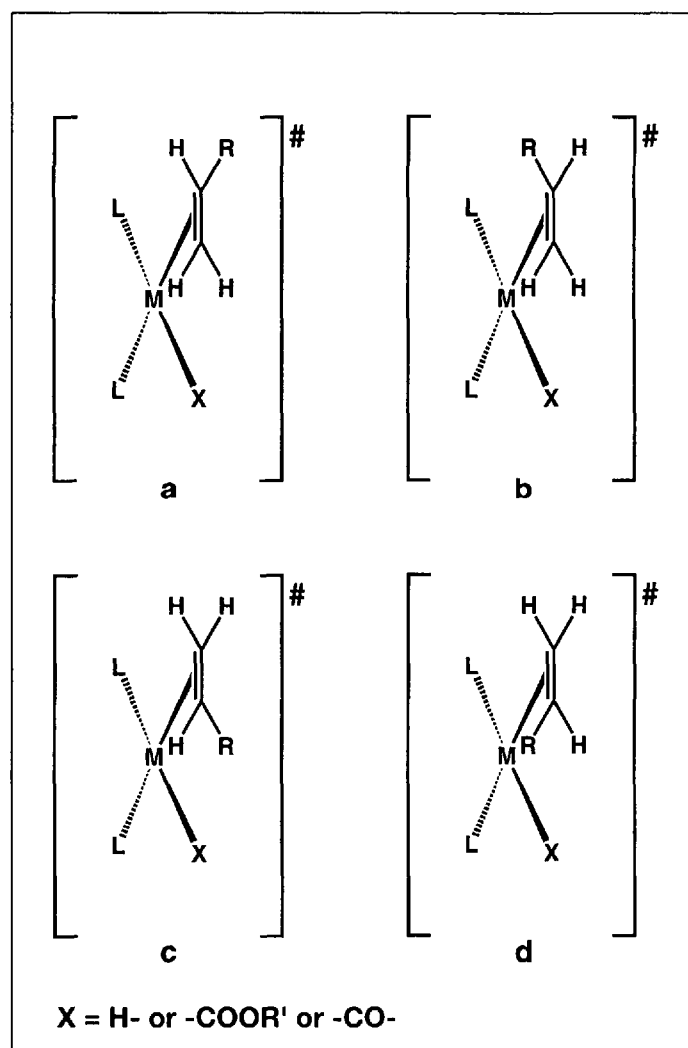


Fig. 2. Four transition states leading to the alkyl complex

ladium-acyl bond seems to be quite general [40]. For aliphatic olefins, the triple carbonylation is non-regioselective, the two regioisomers (Scheme 3, [v]) being formed. However, the enantioselectivity is quite acceptable, at least for one of the two isomers (~80%).

b) Back to Coordination Polymerization. Copolymerization of Olefins with CO

During our investigation of the carbonylation of aliphatic olefins directed towards the synthesis of ketones (Scheme 3, [iii]) using cationic palladium systems modified with propane-1,3-diylbis(diphenylphosphine) we were faced with the problem of the chemoselectivity. As a matter of fact, we always observed the formation of oligomeric materials in the reaction [37]. Those materials were the result of a strictly alternating copolymerization of the olefin with CO (Scheme 3, [vi]), which took place with no regio- and diastereoselectivity [37]. The investigation of the related copolymer of ethene with CO was very lively [41][42], and, in fact, this material will be commercialized on a large scale, starting from this year, under the name *Carilon*[®] [43].

I recognized the opportunity to reconcile our experience in enantioselective carbonylation reactions with our previous approach towards diastereoselective polymerization. In fact, in contrast to polyolefins, copolymers of α -olefins with CO are chiral due to the presence of true asymmetric centres in the macromolecular chain (Fig. 3). A problem we could have anticipated at the beginning of our research was related to the low ability for enantioface selection of aliphatic olefins by the possible ligands to be used in this carbonylation reaction.

However, we did, fortunately, soon recognize the factors responsible for a regioselective enchainment of the aliphatic olefin, namely the basicity of the ligand [44]. Steric effects were much less important [45]. We achieved regioselective copolymerization, since the basic ligands (e.g., propane-1,3-diylbis(diethylphosphine)) cause consecutive primary insertions of the aliphatic olefin. The regioregularity of the growth is accompanied by a fair but still incomplete control of the stereoregularity of the chain towards an isotactic enchainment.

The successive step towards an almost complete stereocontrol was soon done because we were kindly helped by colleagues at *Hoffmann-La Roche* who supplied us with chiral ligands having the required characteristic of basicity. In fact,

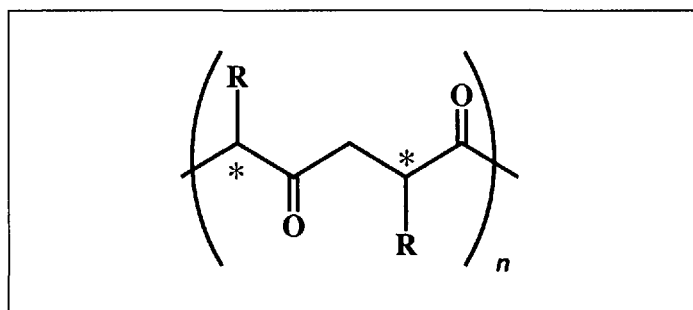


Fig. 3. Asymmetric centers in the macromolecular chain

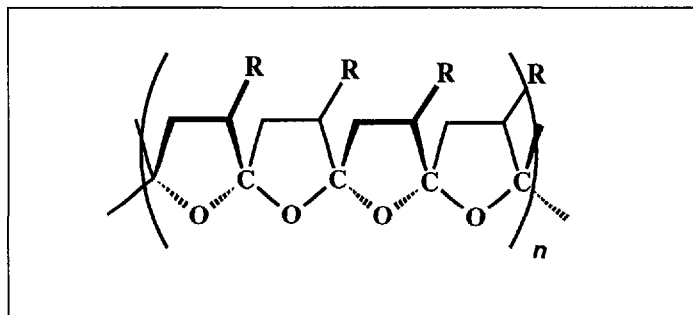


Fig. 4. Spiro ketal structure of copolymer

using optically pure (6,6'-dimethyl-1,1'-biphenyl-2,2'-diyl)bis(dicyclohexylphosphine) we could synthesize the first optically active regio- and stereoregular alternating copolymer of CO with an olefin using propene as the substrate [46][47]. Successive reports by other authors have shown that enantioface selection during the whole copolymerization process should have been very high [48] on the basis of the chiroptical properties of the material. Most surprising was the discovery that the copolymer grows completely in a spiroketal structure (Fig. 4) [49]. The structure had already been observed, but never as the only structure for the copolymers [50].

It has been a challenging, intellectual exercise to propose a new mechanism to account for that structure [49], since we still do not have any experimental findings to fully explain the formation of that structure. More recent investigations by others [48] and by ourselves [51] show that the structure is probably formed after the formation of the polyketone structure, possibly as a consequence of the acidic nature of the catalysts involved; furthermore, the structure does not seem to be regular from the point of view of atropisomerism. In the meantime, we synthesized the highly stereoregular optically active copolymer of other aliphatic olefins such as but-1-ene, 4-methylpent-1-ene and allylbenzene [51]. Other groups later reported the regioregular enantioselective copolymerization of propene and other olefins [48][52] following a similar approach.

In spite of the fact that enantioselectivity in carbonylation reactions of aliphatic olefins is never very high, we, rather eas-

ily, synthesized isotactic copolymers with very high enantioface selection. This was possible since enantioface discrimination during copolymerization is not only influenced by the catalyst being enantiomeric but also by the chain end. Both factors share in determining the stereoselectivity of the reaction, as demonstrated by the chiroptical properties of the copolymer of propene or of but-1-ene and of the corresponding terpolymers containing ethene at high molar ratios ethene/1-olefin [51][53]. Similarly, a double stereodifferentiation was demonstrated in the enantioselective codimerization of propene and CO to the isomeric 2,5-, 3,5-, and 2,6-dimethyl-substituted dimethyl 4-oxoheptanedioates [54].

A chiral alkyl-diphosphine ligand causes an isotactic enantioselective copolymerization; on the other hand achiral diphosphine ligand causes copolymerization with partial isotacticity due to a chain end control. How then does one produce atactic regioregular copolymers? The only way appeared to be the use of chiral ligands having more elements of chirality in order to arrive at a 'confused' information for enantioface selection during the copolymerization process. Using this approach we were indeed able to produce a regioregular propene copolymer having essentially no tacticity [53].

Conclusion

Carbonylation reactions of olefins, in spite of having been studied for many years, still deserve investigation since they

can produce, in a single step, enantiomerically enriched compounds, whose classic synthesis would be very difficult. As previously discussed, all the reactions shown in *Scheme 3* but [iii] were realized enantioselectively. Preliminary results seem to show that this reaction too can be used to prepare optically active compounds. We hope that we will be able to transform our enantiomerically pure copolymers according to *Bayer-Villiger* oxidation. This would open an easy entry to the very important class of polyhydroxy-alkanoates that are interesting polymeric materials also because of their biodegradability.

The preparation of olefin-carbon monoxide copolymers will surely provide us with some more amusement. Open problems are the isotactic enantioselective copolymerization of styrene, as far as the catalytic activity is concerned, and the syndiotactic specific copolymerization of propene and other aliphatic olefins which is still unknown.

I believe that my activity in asymmetric catalysis was facilitated by the contemporary investigation on the stereochemistry of simply metallorganic reactions on transition-metal complexes [55][56]. I hope that the 'divertimento' will continue in both fields over the next few years.

This study would not have been possible without the fine work of collaborators whose names appear in the references and without the help of colleagues working in industry, who supported us financially and by providing us with ligands. I feel profoundly indebted to my former colleague, Dr. A. Stefani, with whom I shared my first experiences in the stereochemistry of homogeneous transition-metal catalysis, to Prof. F. Morandini for fruitful collaboration in the stereochemical investigation of transition-metal complexes, and to the late Prof. P. Pino for his teaching that polymers are matrices which maintain the traces of their chemical history. Finally, I acknowledge financial support of the ETH-Zürich, and of the Swiss National Science Foundation.

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