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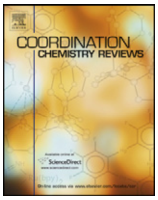

Review

Well-defined transition metal complexes with phosphorus and nitrogen ligands for 1,3-dienes polymerization

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ABSTRACT

This article provides an overview on recent progress in the polymerization of 1,3-dienes catalyzed by transition metal complexes with phosphorus and nitrogen ligands. Polymers having different microstructures (*cis*-1,4; 1,2; mixed *cis*-1,4/1,2) and tacticity (iso- or syndiotactic) were obtained from various 1,3-dienes (1,3-butadiene, isoprene, 1,3-pentadienes, 1,3-hexadienes) depending on the catalyst used, clearly suggesting that the catalyst structure (*i.e.* metal nature, type of ligand) strongly affects the polymerization chemo- and stereoselectivity. However, as indicated by the results obtained in the polymerization of substituted butadienes, a fundamental role in determining the selectivity is also played by the type of

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Abbreviations: acac, acetylacetonate; B, butadiene; bipy, 2,2′-bypiridine; ^{i}Bu, *iso*-butyl; ^{n}Bu, *normal*-butyl; ^{t}Bu, *tert*-butyl; Cy, cyclohexyl; Cyp, cyclopentyl; Cp, cyclopentadienyl; dcpe, 1,2-bis(dicyclohexylphosphino)ethane; depe, 1,2-bis(diethylphosphino)ethane; depp, 1,3-bis(diethylphosphino)propane; 4,7-DiMephen, 4,7-dimethyl-1,10-phenanthroline; 5,6-DiMephen, 5,6-dimethyl-1,10-phenanthroline; 2,9-DiMephen, 2,9-dimethyl-1,10-phenanthroline; 4,7-DiPhphen, 4,7-diphenyl-1,10-phenanthroline; DMB, dimethylbutadiene; dmeda, NN′-dimethylethylendiamine; dmpe, 1,2-bis(dimethylphosphino)ethane; dmpm, bis(dimethylphosphino)methane; dppa, bis(diphenylphosphino)amine; dppe, 1,2-bis(diphenylphosphino)ethane; dppf, 1,1′-bis(diphenylphosphino)ferrocene; dppm, bis(diphenylphosphino)methane; dppp, 1,3-bis(diphenylphosphino)propane; EASC, ethylaluminum sesquichloride; DSC, differential scanning calorimetry; Et, ethyl group; EP, *E*-1,3-pentadiene; GPC, gel permeation chromatography; H, 1,3-hexadiene; HMDS, hexamethyldisilazane; I, isoprene; IR, infrared spectroscopy; L, ligand; MAO, methylaluminoxane; Me, methyl; 5-Mephen, 5-methyl-1,10-phenanthroline; 4-Mephen, 4-methyl-1,10-phenanthroline; Mt, metal atom; NMR, nuclear magnetic resonance; Ph, phenyl group; py, pyridine; ^{i}Pr, *iso*-propyl; ^{n}Pr, *normal*-propyl; phen, 1,10-phenanthroline; tmeda, NNN′N′-tetramethylethylendiammine; 3MP, 3-methyl-pentadiene; 3,4,7,8-TMephen, 3,4,7,8-tetramethyl-1,10-phenanthroline; PI, phenoxyimine; ^{n}Pr, *normal*-propyl; R, alkyl group; T_g, glass transition temperature; T_m, melting temperature.

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Chemoselectivity
Stereoselectivity
Polybutadiene
Polyisoprene
Polypentadiene
Cobalt
Iron
Chromium
Titanium
Nickel
Phosphorus ligands
Nitrogen ligands

monomer: polymers with different structure, some of them completely new, were obtained from different monomers with the same catalyst. All these observations permitted to confirm, and in some cases to improve, the knowledge on the diene polymerization mechanism.

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1. Introduction

Conjugated diolefins can generate several types of polymers having different structures: *trans*-1,4; *cis*-1,4; 1,2 and, in the case of asymmetric monomers (*e.g.* isoprene), 3,4 (Fig. 1). Moreover, isotactic or syndiotactic isomers can be obtained in the case of *cis*-1,4- and *trans*-1,4-polymers when an asymmetric carbon is present in the polymer chain (*e.g.* polymers from 1,3-pentadiene) (Fig. 2). Stereoregular 1,2- or 3,4-polydienes may also exhibit iso- or syndiotacticity and, depending on the structure of the monomer, the double bond in the side chain may present a *trans* or a *cis* configuration (Fig. 3).

1,3-Dienes can be polymerized in different ways, by radical, cationic and stereospecific polymerization. The stereospecific polymerization, differently from the other two methods, is characterized by (i) high chemoselectivity, *i.e.* it can generate polymers having only one type of monomeric unit (1,4; 1,2 or 3,4) and (ii) high stereoselectivity, *i.e.* it can generate polymers with a very high configurational order when steric isomerism sites are present on the monomeric unit (*e.g.* an internal double bond, an asymmetric carbon).

The polymerization of 1,3-dienes with Ziegler–Natta catalysts began in 1954 [1], just after the first results obtained in α-olefin polymerization (Table 1). The first catalysts used were obtained by combining $TiCl_4$ or $TiCl_3$ with aluminum-alkyls, the catalyst systems already used for the polymerization of ethylene and propylene.

The first stereoregular polydiene synthesized was a polyisoprene with a structure very similar to that of natural rubber [16], and it was immediately followed by a polyisoprene with a structure very close to that of gutta-percha [17]. Successively, many other catalytic systems, obtained by combining transition metal (*e.g.* Ti, V, Cr, Fe, Co, Ni) compounds or lanthanide (*e.g.* Nd, Pr) compounds with suitable alkylating agents (*e.g.* $AlEt_3$, $AlEt_2Cl$), were proposed and examined, leading to a breakthrough in the field of conjugated diolefin polymerization [1,18,19]. Four stereoregular polymers were obtained from 1,3-butadiene, having a *trans*-1,4, *cis*-1,4, isotactic 1,2 and syndiotactic 1,2 structures, respectively; several other stereoregular polymers were obtained from terminal substituted butadienes ($CH_2{=}CH{-}CH{=}CHR$; R = alkyl group) and disubstituted

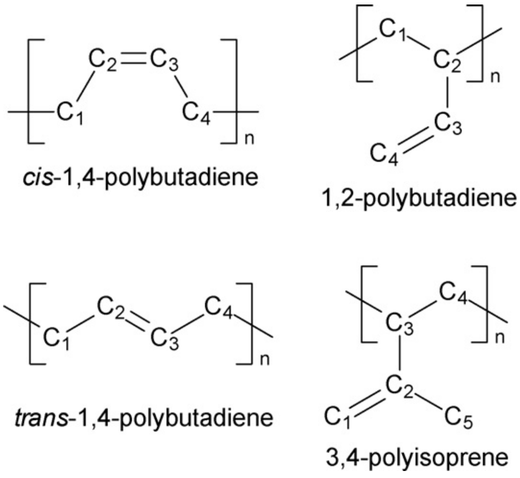

Fig. 1. Polymer microstructures of *cis*-1,4-polybutadiene, *trans*-1,4-polybutadiene, 1,2-polybutadiene and 3,4-polyisoprene.

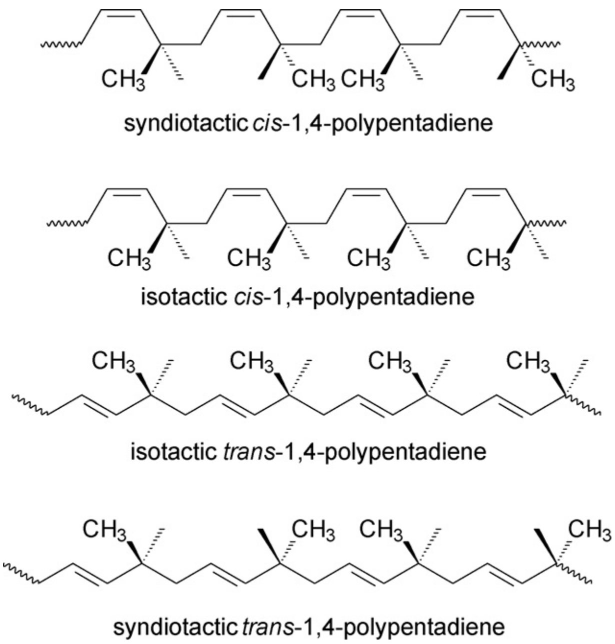

Fig. 2. Possible 1,4-polymers from 1,3-pentadiene.

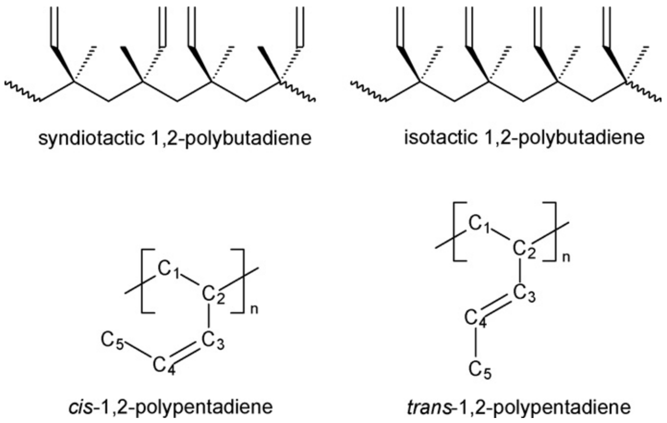

Fig. 3. Polymer microstructures of syndiotactic and isotactic 1,2-polybutadienes, *cis*- and *trans*-1,2-polypentadienes.

Table 1
Polymerization of 1,3-butadiene with Ziegler–Natta catalysts.

Catalyst system and polymerization conditions	Polybutadiene microstructure			Ref.
	cis-1,4 (%)	*trans*-1,4 (%)	1,2 (%)	
Al(^{i}Bu)$_3$–TiI$_4$ (4–5:1) in benzene at 30 °C	92–93	2–3	4–6	[2]
AlEt$_2$Cl–CoCl$_2$·py–H$_2$O (1000:1:100) in benzene at 5 °C	98	1	1	[3]
AlEt$_3$–Ni(octanoate)–BF$_3$·OEt$_2$ (17:1:15) in benzene at 50 °C	96–97	2–3	1	[4]
Al(^{i}Bu)$_3$–NdCl$_3$·*n*L in cyclohexane at 50 °C (L = electron donor)	97	2.7	0.3	[5]
AlEt$_3$–VCl$_3$ (2:1) in heptane at 15 °C		99–100		[6]
AlEt$_2$Cl–VCl$_3$·3THF in toluene at −20 °C		99–100		[7]
AlEt$_3$–Ti(OR)$_4$ (ca. 7:1) in heptane at 0–15 °C			≥90	[8]
AlEt$_3$–V(acac)$_3$ (6–10:1) in benzene at 15 °C			80–86	[9]
AlR$_3$–Mo(acac)$_3$ (4–5:1) in benzene at 40 °C			≥90	[10]
AlR$_3$–Co(acac)$_3$–CS$_2$ (50:1) in benzene at 40 °C			99–100	[11–14]
AlR$_3$–Cr(CNPh)$_6$ (2–15:1)in benzene at 15 °C			80–85	[15]

butadienes [*e.g.* $CH_2{=}C(Me){-}C(Me){=}CH_2$; $CH_2{=}CH{-}CH{=}CMe_2$; $CH_2{=}C(Me)CH{=}CH(Me)$; $CH(Me){=}CH{-}CH{=}CH(Me)$]. Some examples of the catalyst systems used for butadiene polymerization are reported in Table 1; more detailed information on catalysts and polymers can be found on some already published reviews on this topic [1,18,19].

With the discovery of methylaluminoxane as an alkylating agent, at the beginning of the1980s [20,21], novel catalytic systems were introduced in the field of conjugated diolefin polymerization (Table 2) [22–28]. These novel catalysts were in some cases more active and stereospecific than those previously known and based on common aluminum-alkyls. Specifically, MAO permitted to use, as catalyst precursors, cyclopentadienyl transition metal compounds (*e.g.* $CpTiCl_3$, Cp_2TiCl_2, $CpVCl_2$) [29–34], obtaining extremely active catalytic systems able to polymerize also monomers such as *Z*-1,3-pentadiene [35–37] and 4-methyl-1,3-pentadiene [29,31–34,38], which were not polymerized with the common Ziegler–Natta catalysts.

A breakthrough in the field of olefin polymerization occurred at the beginning of the 1990s, the discovery, by both academic and industrial groups, of a new generation of catalyst based on transition metal complexes with a wide range of ligands having N, P, O or other donor atoms [39–54]. In particular, the discovery of new olefin polymerization catalysts based on late transition metals represented a major advance. The study of late transition metal complexes (*e.g.* Fe, Co, Ni, Pt, Pd) rose from the attempts to find catalysts able to give incorporation of polar monomers. Early transition metal metallocene or Ziegler–Natta catalysts are highly sensitive to polar reagents due to their strong Lewis acid character, thus a polar comonomer can be used only if, for instance, their polar groups are protected. Late transition metal complexes have a lower Lewis acid character, resulting in weaker, reversible coordination of polar substances and much higher tolerance to the presence of polar functionalities or solvents.

The use of the late transition metal catalysts in olefin polymerization has led to different polymer structures and unique properties other than those existing, even in the well-studied field of ethylene homo- and co-polymerization. Among the major discoveries, we can mention: (i) perfectly alternating olefin/carbon monoxide co-polymers obtained with catalysts based on palladium(II) complexes with bidentate chelating phosphorus or nitrogen ligands [39,40]; (ii) the introduction, by Brookhart and co-workers in the mid-1990s, of highly active nickel(II) and palladium(II) complexes of α-diimine ligands capable of polymerizing ethylene to either linear or highly branched polyethylene, depending on the ligand backbone and reaction conditions (without special ligands, late transition metals usually yield dimers or oligomers of olefins, due to their tendency to give chain transfer by β-hydride elimination) [41,42]; (iii) the discovery that iron and cobalt complexes with iminopyridine ligands show high activities for ethylene polymerization giving strictly linear, high molecular weight polymers or α-olefin oligomers depending on steric bulkiness of the substituents on the imino nitrogen of the ligand [43–49]; (iv) the introduction of phenoxyimine (PI) complexes of zirconium, titanium, vanadium and nickel. The PI titanium complexes produced polyethylene with a narrow molecular weight distribution, whereas the PI vanadium complexes were one of the first examples of vanadium-based single-site catalysts in the olefins homo- and co-polymerization [50], after the VCl_4-based catalysts for the polymerization of propene reported by Zambelli [55,56], and the $V(acac)_3$-based catalysts for the living homo- and co-polymerization of propene and ethene reported by Doi [57,58]. PI nickel(II) precursors were able to homo- and co-polymerize ethylene with polar monomers such as vinylethers and methacrylates [51–54].

A similar breakthrough was achieved in the 1,3-dienes polymerization by using catalysts based on transition metal (mainly Cr, Fe, Co) complexes with phosphorus and nitrogen ligands in combination with MAO. These systems were extremely active and allowed one to modulate the polydiene microstructure (*cis*-1,4; 1,2; mixed *cis*-1,4/1,2 structure with variable 1,2 content) by varying the type of ligand and metal [59–76]. The same catalysts were also able to give novel highly stereoregular polymers from different types of substituted butadienes (*e.g.* isoprene, 1,3-pentadiene, 1,3-

Table 2
Polymerization of 1,3-butadiene with MAO-transition metal compound-based catalysts.

Catalyst system	Polybutadiene microstructure			Ref.
	cis-1,4 (%)	*trans*-1,4 (%)	1,2 (%)	
Ti(O^{n}Bu)$_4$–MAO (1:1000) in toluene at 15 °C	93.0	3.3	3.7	[22,24]
V(acac)$_3$–MAO (1:1000) in toluene at 15 °C		≥97		[22,23,25]
Co(acac)$_3$–MAO (1:1000) in toluene at 15 °C	96.4	2.4	1.2	[22]
Nd(OCOC$_7$H$_{15}$)$_3$–MAO (1:1000) in toluene at 15 °C	94.6	3.6	1.8	[22]
CpTiCl$_3$–MAO (1:1000) in toluene at 20 °C	81.4		18.6	[29,32–34]
(C$_5$H$_4$Me)VCl$_2$·(PEt$_3$)$_2$–MAO (1:1000) in toluene at 25 °C	80.4	2.4	17.2	[30]
Cp$_2$TiCl$_2$–MAO (1:1000) in toluene at 25 °C	~80			[31–33]
Cp$_2$TiCl–MAO (1:1000) in toluene at 25 °C	~80			[31–33]
Cp$_2$VCl–MAO (1:1000) in toluene at 15 °C	84.8	1.8	13.4	[30]

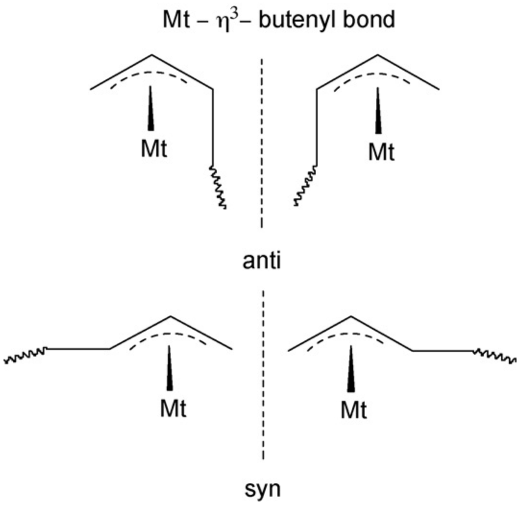

Fig. 4. Bonds between the growing polymer chain and the transition metal of the catalyst in 1,3-diene polymerization.

hexadiene, 3-methyl-1,3-pentadiene) [72,77–81]. Furthermore, their ability to polymerize different types of 1,3-dienes allowed one to support some of the hypotheses previously formulated on the diene polymerization mechanism [1,32,33,75,82–106] and to highlight some novel aspects of the mechanism, such as the influence of the catalyst structure (*i.e.* type of ligand on the metal) and of the monomer structure on the polymerization stereoselectivity.

This paper provides an overview on recent progress in the polymerization of 1,3-dienes with catalysts based on transition metal complexes with phosphorus and nitrogen ligands.

2. Some remarks about the diene polymerization mechanism

As reported above, the results achieved with catalysts based on transition metal complexes with phosphorus and nitrogen ligands, appeared to be helpful for a better diene polymerization mechanism comprehension. For this reason, before discussing the mode of formation of the various polymers, we briefly recall some features of such a mechanism. For a deeper and more detailed information on the diene polymerization mechanism, a careful reading of the various papers by Porri and other authors is recommended [1,75,86,97,106].

In the polymerization of 1,3-dienes, the growing polymer chain is bonded to the metal atom (Mt) through an allylic bond formed by insertion of the monomer on the carbon-metal bond of the catalyst system (Fig. 4); it is worthwhile to note that the Mt-butenyl group is a chiral group.

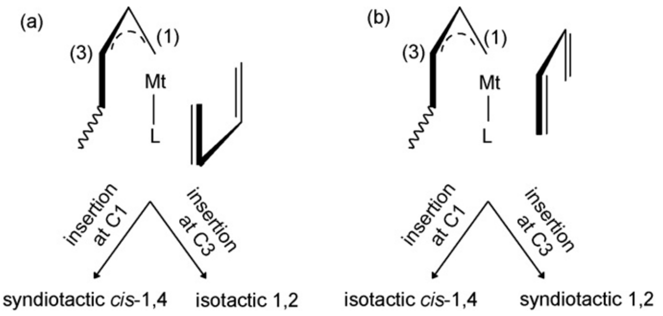

Fig. 6. Possible orientations [(a) *exo–endo* and (b) *exo–exo*] of the new incoming monomer with respect to the last-inserted unit (L is a generic ligand) and formation of *cis*-1,4 and 1,2-polymers having a syndiotactic or an isotactic structure.

According to the polymerization mechanism proposed by Porri, the allylic unit can exist in two forms (*anti* and *syn*) (Fig. 4) both exhibiting two reactive positions: C1 and C3 (Fig. 5). When the new entering monomer reacts at C1, a 1,4 unit is formed (*cis* if the allylic unit is in the *anti* form, *trans* if the allylic unit is in the *syn* form), whereas a 1,2 unit is obtained if the incoming monomer reacts at C3 (Fig. 5).

Furthermore, the new incoming monomer can orient in two different ways with respect to the allylic unit of the polymer growing chain, as in Fig. 6(a) (*exo–endo*) or as in Fig. 6(b) (*exo–exo*) (for simplicity we have reported only the case of the *anti* unit, but the same is valid in the case of the *syn* unit).

From a situation as in Fig. 6(a), *cis*-1,4 syndiotactic or 1,2 isotactic units are formed if the monomer reacts at C1 or C3, respectively; from a situation as in Fig. 6(b), we have instead the formation of *cis*-1,4 isotactic units if the monomer reacts at C1, and of 1,2-syndiotactic units if the monomer reacts at C3.

3. Chromium catalysts

Chromium catalysts are well known for giving 1,2-polymers from 1,3-butadiene [15,107,108]. For instance, the system Cr(acac)$_3$–AlEt$_3$ gave a 1,2-polybutadiene with a syndiotactic or an isotactic structure depending on the polymerization conditions (*e.g.* Al/Cr molar ratio) [15]; the activity of this system was however rather low. More active and stereospecific catalysts have been recently obtained by combining Cr(II) phosphine complexes (CrCl$_2$·L$_n$; L = bidentate phosphines; n = 1, 2) with MAO [70,74,109–111].

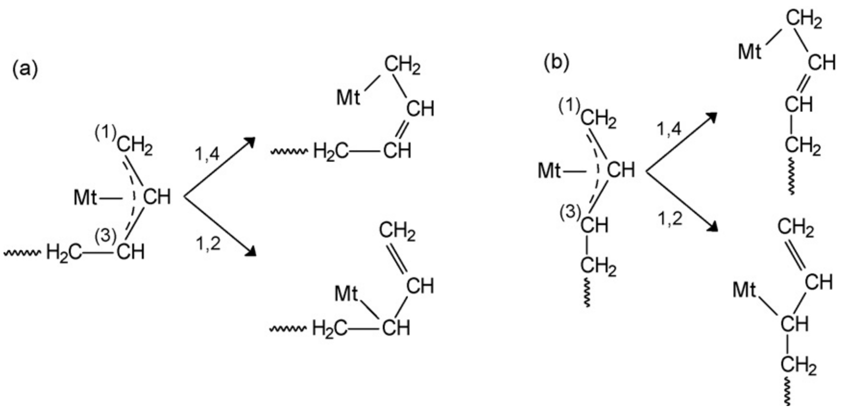

Fig. 5. Formation of 1,4 *vs* 1,2 monomeric units from (a) *anti* and (b) *syn* Mt-butenyl group.

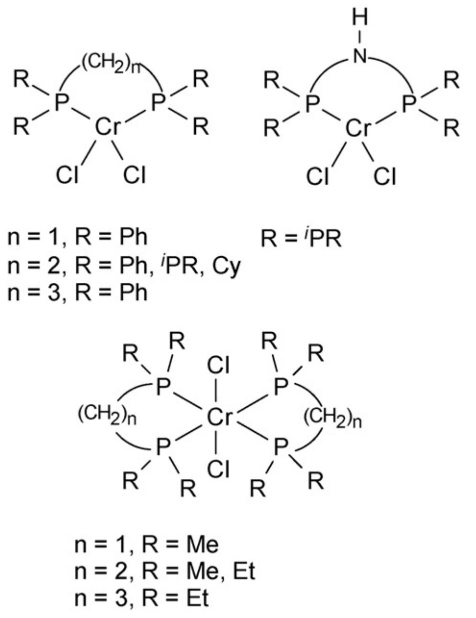

Fig. 7. Cr(II) complexes with bidentate phosphines.

3.1. Synthesis of chromium phosphine complexes

The bidentate phosphine Cr(II) complexes were prepared by reacting $CrCl_2{\cdot}2THF$ with a bidentate phosphine in toluene or diethylether as solvent; several complexes were obtained (Fig. 7) and for some of them the crystal structures were also determined (Fig. 8) [70,74,109–111].

3.2. Homo- and co-polymerization of 1,3-dienes

The above phosphine chromium complexes were used in combination with MAO for the polymerization of 1,3-butadiene. They were extremely active, giving predominantly 1,2-polybutadiene (1,2 content >85%) having different tacticity (syndiotactic or predominantly isotactic) depending on the phosphine ligand bonded to the chromium atom (Table 3) [59,60,70,74,76]. It is well known that phosphine steric and electronic properties are strongly affected by the type and nature of the substituents on the phosphorus atom [112–115].

A relationship between stereoselectivity and phosphine ligand bulkiness was suggested: isotactic 1,2-polybutadienes were obtained with catalysts with minimally hindered phosphines (*e.g.* $CrCl_2(dmpm)_2$–MAO; $CrCl_2(dppm)$–MAO) while highly syndiotactic 1,2-polymers were obtained with catalysts with more hindered ligands (*e.g.* $CrCl_2(dmpe)_2$–MAO; $CrCl_2(depe)_2$–MAO; $CrCl_2(dppa)$–MAO) (Fig. 9). With much more hindered phosphines (*e.g.* $CrCl_2(depp)_2$–MAO; $CrCl_2(dppp)$–MAO; $CrCl_2(dcpe)$–MAO), predominantly 1,2-syndiotactic polymers were still obtained, but with a lower 1,2 content (70–80%), meaning that the type of ligand has also some influence on chemoselectivity.

The formation of 1,2-polybutadienes having different type and degree of tacticity (iso- and syndiotactic) upon the phosphine ligand has been interpreted on the basis of the diolefin polymerization mechanism previously proposed [1,75,86,97,106].

By assuming that the catalytic site is that shown in Fig. 10(a), with only one bidentate phosphine on the metal, when the new monomer reacts at C3 of the allylic unit a 1,2 unit is formed: if the monomer and the allylic unit are *exo–exo* oriented, a syndiotactic dyad is obtained; if they are *exo–endo* oriented, an isotactic dyad is formed. Most probably in the case of more hindered ligands (*e.g.* dmpe, depe, depp) the *exo–exo* orientation is much more favored and 1,2-syndiotactic sequences are formed; in the case of less hindered ligands (*e.g.* dmpm) both orientations are possible, being the *exo–endo* one more favored, and predominantly isotactic

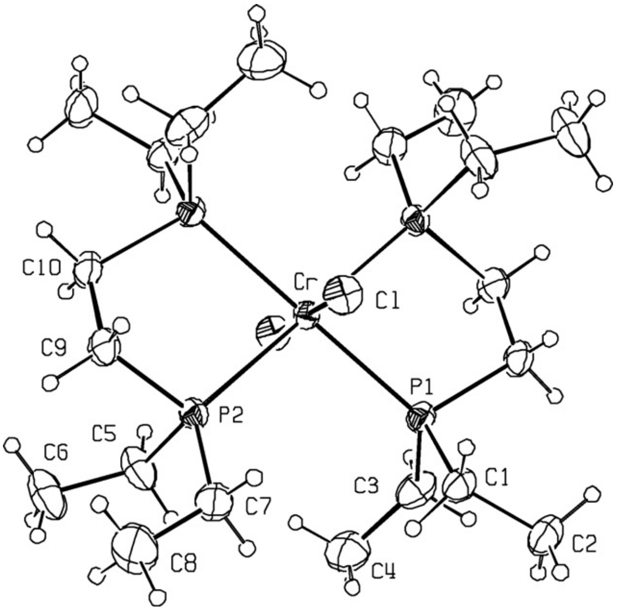

Fig. 8. $CrCl_2(depe)_2$ X-ray crystal structure [70].

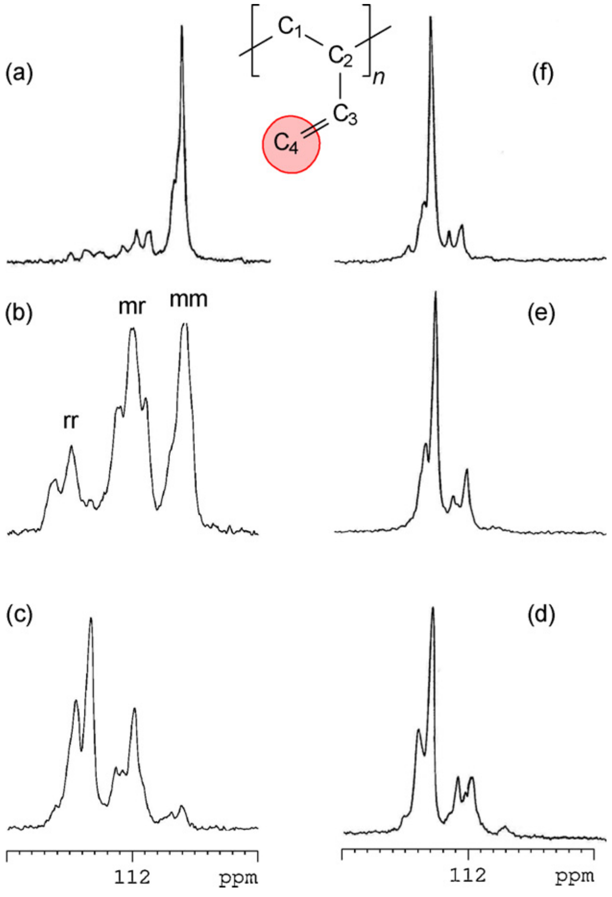

Fig. 9. ^{13}C NMR spectra ($C_2D_2Cl_4$; HMDS as internal standard; 103 °C; olefinic region, C4 signal) of 1,2-polybutadienes obtained with (a) $CrCl_2(dmpm)_2$–MAO; (b) $CrCl_2(dppm)$–MAO; (c) $CrCl_2(dppe)$–MAO; (d) $CrCl_2(dppa)$–MAO; (e) $CrCl_2(depe)_2$–MAO; (f) $CrCl_2(dmpe)_2$–MAO [59,70,74].

Table 3
Polymerization of 1,3-butadiene with Cr(II) phosphine complexes-based catalysts [59,70,74].

Cr compound	Polymerization[a]		Polymer microstructure[b]			m.p.[c] (°C)
	Time (h)	Conv. (%)	*cis*-1,4 (%)	1,2 (%)	*rr*/*mr*/*mm* (%)	
$CrCl_2(dmpm)_2$	1/2	80.2	10.7	89.3	16/13/71	[d]
$CrCl_2(dmpe)_2$	1	39.5	5.0	95.0	83/17/0	152
$CrCl_2(depe)_2$	1	76.0	10.9	89.1	72/26/2	106
$CrCl_2(depp)_2$	2.7	31.1	15.2	84.8	67/30/3	104
$CrCl_2(dcpe)$	1110	5.9	34.0	66.0		[d]
$CrCl_2(dppm)$	1/3	55.7	11.0	89.0	17/13/70	[d]
$CrCl_2(dppe)$	1020	15.3	12.0	88.0	61/34/5	95
$CrCl_2(dppp)$	1440	17.6	20.0	80.0	64/32/4	106
$CrCl_2(dppa)$	1/12	37.5	9.0	91.0	66/30/4	104

[a] *Polymerization conditions*: butadiene, 2 mL; toluene, total volume 16 mL; MAO, Al/Cr = 1000; 1×10^{-5} mol of Cr; 20 °C.
[b] Determined by ^1H and ^{13}C NMR analysis.
[c] Melting point, determined by DSC analysis.
[d] Melting point not observed.

sequences containing a certain amount of steric errors are formed [59,70,74].

The polymerization of isoprene with the system $CrCl_2(dmpe)_2$–MAO was also investigated; a predominantly 3,4-polymer, amorphous by X-ray and characterized by a low stereoregularity (Fig. 11), was obtained [59].

The lack of stereoregularity of the polyisoprene obtained with $CrCl_2(dmpe)_2$–MAO (the same system gave a highly syndiotactic polymer from butadiene) was attributed to the strong steric interaction between the new monomer and the allylic group [59], because of the methyl groups (Fig. 10(b)). The steric interaction may favor the formation of an *exo–endo* situation, in addition to the *exo–exo* one. Both orientations become possible, the *exo–exo* arrangement leading to a 3,4-syndiotactic dyad, the *endo–exo* one leading to an isotactic dyad, and indeed an atactic polymer is formed.

The co-polymerization of butadiene with isoprene using the system $CrCl_2(dmpe)_2$–MAO was also reported; co-polymers in which the butadiene units have a 1,2 structure and the isoprene units a 3,4 structure were obtained, with a melting point decreasing with increasing the isoprene content (Table 4) [60].

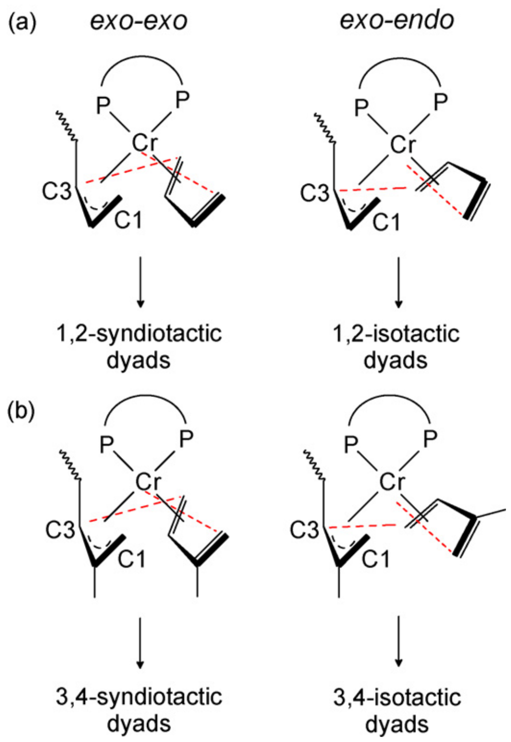

Fig. 10. Possible active site structures in the polymerization of (a) 1,3-butadiene and (b) isoprene.

Various catalysts have been proposed, in the patent literature, for the preparation of syndiotactic 1,2-polybutadiene having a controlled degree of stereoregularity [116–124]. The co-polymerization of butadiene with a small amount of isoprene provides a convenient route to this type of products.

4. Iron catalysts

Iron catalysts have not been extensively studied in the field of conjugated diolefin polymerization and only a few papers have been published concerning the homo- and co-polymerization of butadiene and isoprene with the catalytic system obtained by mixing $Fe(acac)_3$, $Al(^iBu)_3$ and 1,10-phenanthroline (phen) [125]. This system was reported to have a low activity and a poor stereoselectivity: it gave a polybutadiene with a mixed *cis*-1,4/1,2 structure and a polyisoprene with a predominantly 3,4 structure. The active species in this catalytic system, as suggested by the authors, was probably a phenanthroline iron(II) complex originating from the reduction of $Fe(acac)_3$ by the aluminum-alkyl.

Few recent papers have been reported concerning the cyclodimerization [126–128] and the polymerization of 1,3-dienes (*e.g.* butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 3-methyl-1,3-pentadiene) [61–63,65] with catalysts obtained by combining various iron diethyl or dichloride complexes with aliphatic and aromatic bidentate amines (Fig. 12) [62,65] and aluminum-alkyls ($Al(^iBu)_3$, $Al(Et)_3$, MAO).

Catalyst activity, chemo- and stereoselectivity of the above systems are strongly influenced by the type of ligand (Table 5) [61–63,65]. Specifically, systems based on iron complexes with aromatic bidentate amines (*e.g.* 2,2′-bipyridine or 1,10-phenanthroline) exhibited an extremely high activity, giving an essentially 1,2-syndiotactic polymer from butadiene. Catalysts based on aliphatic amines were characterized by a low activity and stereospecificity, whereas catalysts based on iron dichloride and its complexes with bidentate phosphines were practically inactive.

These systems were also highly active in the polymerization of various substituted butadienes (*e.g.* isoprene, 2,3-dimethyl-1,3-butadiene, 3-methyl-1,3-pentadiene) giving novel, highly stereoregular polymers (Table 6) [61–64,79,80,129].

Specifically, the systems $FeCl_2(bipy)_2$–MAO and $FeEt_2(bipy)_2$–MAO gave a crystalline *cis*-1,4-polymer from 2,3-dimethyl-1,3-butadiene [61,62,129], with a melting point of about 200 °C; such a polymer had been obtained only with the systems $CpTiCl_3$–MAO [29] and $AlEt_2Cl$-$Nd(OCOC_7H_{15})_3$–$Al(^iBu)_3$

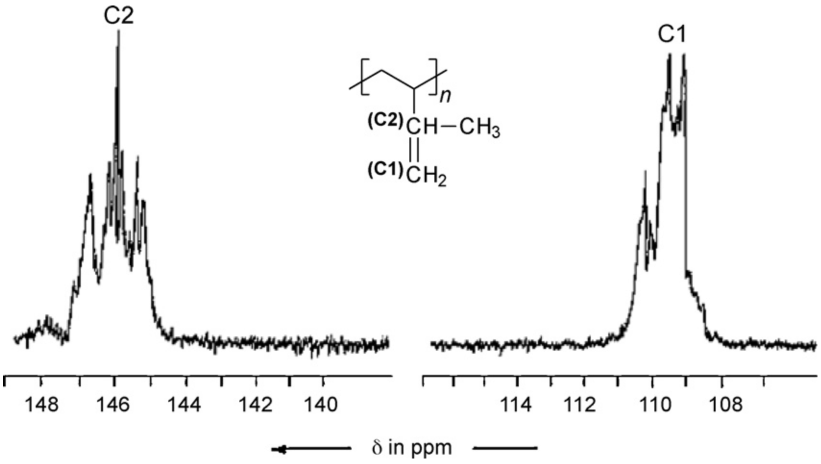

Fig. 11. ^{13}C NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C; olefinic region) of 3,4 atactic polyisoprene obtained with $CrCl_2(dmpe)_2$–MAO [59].

Table 4
Butadiene–isoprene co-polymerization with $CrCl_2(dmpe)_2$–MAO[a] [60].

Feed		Time (min)	Yield		Co-polymer composition[b]		m.p.[c] (°C)	T_g[c] (°C)	rrrr[d] (%)
I (mL)	B:I (mol%)		mg	%	B (mol%)	I (mol%)			
0	100:0	10	214	15.3	100.0	0	162		74.9
1	82:28	15	175	8.3	97.4	2.6	148		67.2
3	46.5:53.5	20	178	5.2	95.4	4.6	128		62.0
6	30:70	153	208	3.8	90.0	10.0	107		55.7
8	24.5/75.5	158	187	3.0	85.3	14.7	89		50.6
10	20.5/79.5	120	474	5.8	83.5	16.5	49		46.2
15	15/85	155	465	4.0	81.0	19.0	52	5	42.0
25	9.5:90.5	243	360	2	68.5	31.5		3	33.4
2	0:100	6840	946	69.6	0	100		29	

[a] *Polymerization conditions*: toluene, total volume 30 mL; butadiene, 2 mL (Cr, 3×10^{-5} mol); Al/Cr = 100; +20 °C.
[b] Determined by NMR analysis; butadiene units have a 1,2 structure while isoprene units a 3,4 structure.
[c] Melting point and glass transition temperature, determined by DSC measurements.
[d] Percentage of syndiotactic pentads, determined by ^{13}C NMR.

[130,131], but the activity of iron catalysts was much higher with respect to the titanium and neodymium catalysts. Moreover, they gave a 3,4-syndiotactic polymer from isoprene [63,64] and a syndiotactic 1,2-polymer from 3-methyl-1,3-pentadiene [79,80] (Fig. 13); these highly stereoregular polymers were never obtained before.

The formation of polymers having a syndiotactic structure from isoprene and 3-methyl-1,3-pentadiene is a further indication of the role played by the ligand in determining the polymerization stereoselectivity. The presence of a bulky ligand on the iron metal favors the *exo–exo* orientation with respect to the *exo–endo* one, with consequent formation of a syndiotactic polymer (Fig. 14).

Table 5
Polymerization of 1,3-butadiene with iron catalysts [62].

Polymerization[a]					Polymer microstructure			
Fe compound		Temp (°C)	Time (min)	Conv. (%)	*cis*-1,4[b] (%)	*trans*-1,4[b] (%)	1,2[b] (%)	rrrr[c] (%)
Type	(×10⁶ mol)							
$FeCl_2$	10	20	1110	–				
$FeCl_2(dmpe)_2$	10	20	1110	–				
$FeCl_2$(tmeda)	10	20	100	10	66.6	6.5	26.9	
$FeCl_2$(dmeda)	10	20	1110	47	63.2	16.0	20.8	
$FeCl_2(phen)_2$	1	20	0.5	100	30.0		70.0	
$FeCl_2$(5-Mephen)$_2$	1	20	1	43	27.0		73.0	
$FeCl_2$(5,6-DiMephen)$_2$	1	20	1	32	30.0		70.0	
$FeCl_2$(4-Mephen)$_2$	1	20	1	22	33.0		67.0	
$FeCl_2$(4,7-DiMephen)$_2$	1	20	3	90	25.0		75.0	
$FeCl_2$(4,7-DiPhphen)$_2$	1	20	3	61	29.0		71.0	
$FeCl_2$(3,4,7,8-TMephen)$_2$	1	20	22	19	35.0		65.0	
$FeCl_2$(2,9-DiMephen)$_2$	1	20	600	15	40.0		60.0	
$FeCl_2(bipy)_2$	1	20	0.5	100	32.5		67.5	36.9
$FeCl_2(bipy)_2$	3	−40	10	20	16.8		83.2	42.5
$FeCl_2(bipy)_2$	3	−78	4200	17	9.0		91.0	52.5

[a] *Polymerization conditions*: butadiene, 2 mL; toluene, total volume 16 mL; MAO, Al/Fe = 1000.
[b] Determined by ^{1}H and ^{13}C NMR analysis.
[c] Percentage of syndiotactic pentads, determined by ^{13}C NMR.

Table 6
Polymerization of 1,3-dienes with $FeCl_2(bipy)_2$–MAO [61,62,79].

Polymerization[a]					Polymer microstructure[b]			m.p.[c] (°C)
Fe (×10^6 mol)	Monomer	Temp (°C)	Time (min)	Conv. (%)	*cis*-1,4 (%)	1,2 (%)	3,4 (%)	
3	I	20	0.5	100	33		67	
3	I	−40	18	14	23		77	
3	I	−78	4200	15	7		93	163
3	EP	20	5	100	30	70		
3	DMB	20	0.5	100	100			200
3	DMB	−40	60	25	100			203
20	3MP	−30	14,400	78		100		242

[a] *Polymerization conditions*: monomer, 2 mL; toluene, total volume 16 mL; MAO, Al/Fe = 1000.
[b] Determined by NMR analysis.
[c] Melting point, determined by DSC analysis.

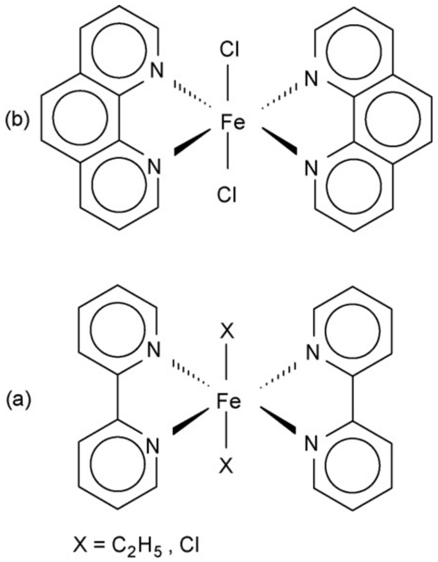

Fig. 12. Iron(II) complexes with (a) 2,2′-bipyridine and (b) 1,10-phenanthroline.

5. Cobalt catalysts

Cobalt catalysts play a very important role in the field of butadiene polymerization since, depending on the reaction conditions and catalyst formulation, they can produce polymers with different microstructure, including *cis*-1,4-polybutadiene and syndiotactic 1,2-polybutadiene (Fig. 1), which are the only two polybutadienes produced on an industrial scale [1,18]. Several cobalt compounds can be used as catalytic precursors to polymerize butadiene to *cis*-1,4-polymer with a *cis* content up to 97–98% [1,18], provided that a suitable cocatalyst (*e.g.* $Co(acac)_3$–$AlEt_2Cl$–H_2O) [132] is used. Equibinary *cis*-1,4/1,2-polybutadiene is instead obtained with the system $Co(acac)_3$–$AlEt_3$–H_2O [133]. Cobalt catalysts (*e.g.* $Co(acac)_3$–$AlEt_3$–H_2O–CS_2; (η^3-C_8H_{13})(η^4-C_4H_6)Co) [11–14,134], however, are also used to prepare syndiotactic 1,2-polybutadiene which, contrary to amorphous *cis*-1,4-polybutadiene, is a crystalline polymer with T_m up to 200–220 °C and a T_g in the range −15/−30 °C.

The effect of the *in situ* addition of mono- and bidentate phosphines to the above cobalt catalysts (*e.g.* Co(2-ethylhexanoate)$_2$–$AlEt_2Cl$–H_2O; $CoCl_2$–$AlEt_3$; $CoCl_2$–MAO) in the polymerization of butadiene was also investigated [135–137]. The phosphine ligand influenced the polymer microstructure; in general a mixture of macromolecules having different structure was obtained, likely due to the formation of different active species as a consequence of the *in situ* phosphine addition.

On the basis of the above results, researchers started to synthesize well-defined cobalt complexes with phosphorus ligands and to investigate their behaviour, in combination with MAO, in the polymerization of 1,3-dienes [71–71,75,138–140]. These novel catalysts were able to manage polybutadiene microstructure, as occurred in the polymerization of α-olefins catalyzed by titanium or zirconium metallocenes [141,142]. Polybutadienes with controlled

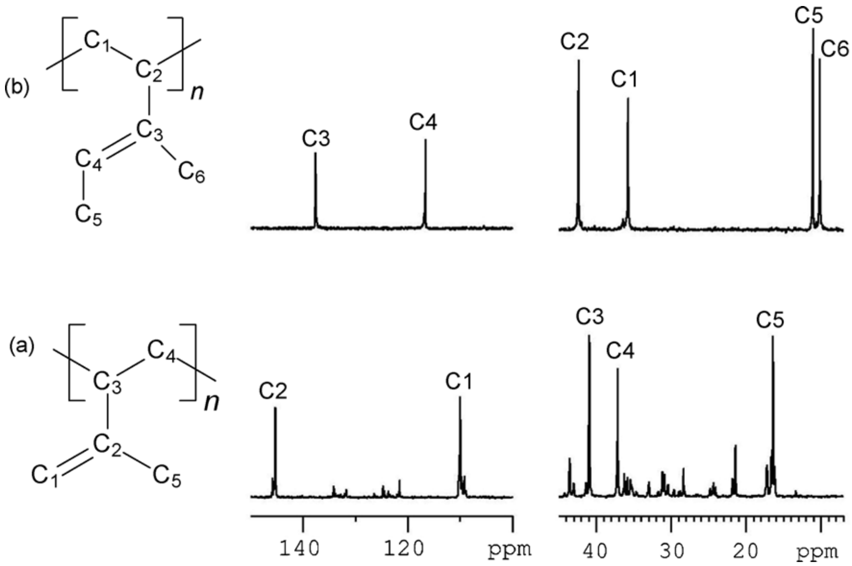

Fig. 13. ^{13}C NMR spectra ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of (a) syndiotactic 3,4-polyisoprene and (b) syndiotactic 1,2-poly(*E*-3-methyl-1,3-pentadiene) obtained with $FeCl_2(bipy)_2$–MAO [61–63,75].

microstructure (*cis*-1,4, linear or branched; 1,2, iso- or syndiotactic; mixed *cis*-1,4/1,2 with variable 1,2 content) were obtained simply varying the type of phosphine bonded to the cobalt atom.

Furthermore, catalysts based on phosphine cobalt complexes polymerize several other substituted butadienes such as isoprene, 1,3-pentadienes and 1,3-hexadienes, giving homo- and co-polymers with different structures from different monomers [72,75,77,78,81].

5.1. Synthesis of cobalt phosphine complexes

The cobalt phosphine complexes were prepared and isolated by reacting anhydrous cobalt dichloride with several aliphatic and aromatic mono- and bidentate phosphines (Fig. 15), using ethanol as solvent [66–69,71–73,75,143].

In some cases single crystals of the phosphine complexes, suitable for X-ray structure determination, were obtained and the crystal structure was reported (Fig. 16) [71–73].

5.2. Polymerization of 1,3-butadiene with $CoCl_2(PR_3)_2$–MAO

The results obtained in the polymerization of butadiene with the systems prepared by combining MAO with various cobalt aliphatic phosphine complexes are reported in Table 7 [71,75]. Predominantly *cis*-1,4-polymers were obtained with catalysts using more hindered ligands, while polybutadienes with a predominantly 1,2 structure or mixed *cis*-1,4/1,2 structure were obtained in the case of less hindered phosphines (Fig. 17). The *cis* content seems indeed to increase with increasing the ligand hindrance.

It is worthwhile to note that polymers with a high *cis*-1,4 content obtained with catalysts using hindered phosphines (*e.g.* P^tBu_3, P^iPr_3, P^tBu_2Me) are reported to be branched, while the system $CoCl_2$–MAO gives a linear high *cis* content polybutadiene; moreover, in the polymers having a mixed *cis*-1,4/1,2 structure, the *cis*-1,4 and 1,2 units are randomly distributed along the polymer chain, suggesting that the phosphine ligand is not displaced by the cobalt atom during the polymerization, and the active site structure is likely that shown in Fig. 18.

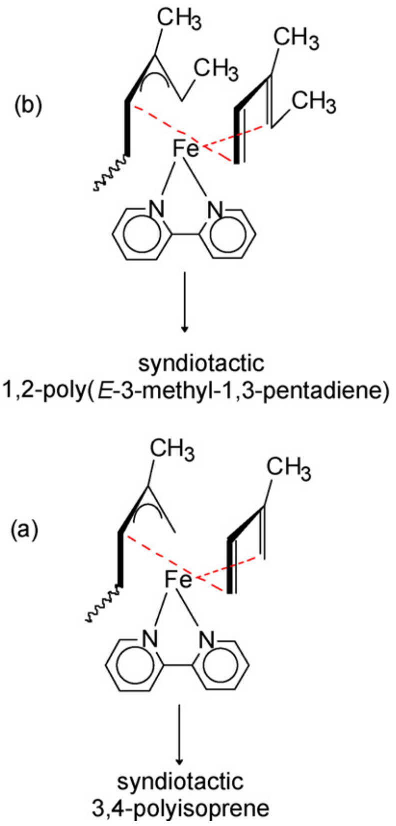

Fig. 14. Formation of syndiotactic (a) 3,4-polyisoprene and (b) 1,2-poly(*E*-3-methyl-1,3-pentadiene) with $FeCl_2(bipy)_2$–MAO.

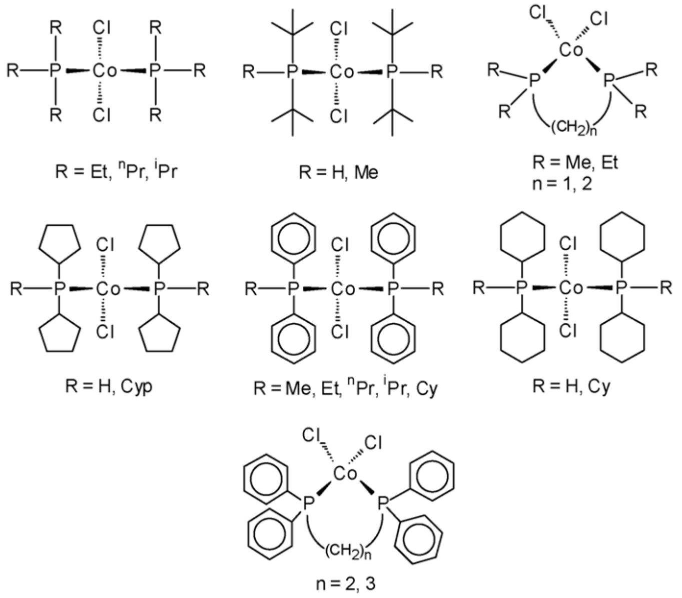

Fig. 15. Cobalt phosphine complexes.

5.3. Polymerization of 1,3-butadiene with bidentate phosphine cobalt complexes

High *cis*-1,4-polymers (around 95%) were also obtained with $CoCl_2[R_2P(CH_2)_nPR_2]$–MAO (R = Me, Et, Ph; n = 1, 2), independently of the cobalt complex used [75].

Since *cis*-1,4-polymers are also obtained with the system $CoCl_2$–MAO, one could think that the bidentate phosphine is displaced from the cobalt atom during the polymerization and that the effective catalyst is that originating from the reaction between $CoCl_2$ and MAO. However, the *cis* polymers obtained with $CoCl_2$–MAO and $CoCl_2[R_2P(CH_2)_nPR_2]$–MAO are different, the former being linear and the latter branched. Similar behavior was previously observed in the polymerization of butadiene with $CoCl_2(PR_3)_2$–MAO in which PR_3 is a hindered phosphine [67].

If we admit that in the active site structure the butenyl group of the growing chain is η^3-bonded, and the incoming butadiene monomer is *cis*-η^4-bonded, only one phosphorus atom can coordinate to the cobalt atom because otherwise, with two phosphorus atoms coordinated, we would have an electron in excess with respect to the rare gas (18e) rule. It follows that in the active site formed in the polymerization of 1,3-butadiene with catalysts based on bidentate phosphine cobalt complexes, the bidentate phosphine likely remains coordinated to the cobalt atom with only one phosphorus atom (Fig. 19). Such a coordination could be in some way responsible for the formation of branched polymers.

5.4. Polymerization of 1,3-butadiene with $CoCl_2(PRPh_2)_2$–MAO and $CoCl_2(PR_2Ph)_2$–MAO

The polymerization of 1,3-butadiene with $CoCl_2(PRPh_2)_2$–MAO was also examined [68,69,72,73,75]; these systems were extremely active in the polymerization of butadiene and a complete monomer conversion was reached in a few minutes. The polymers obtained

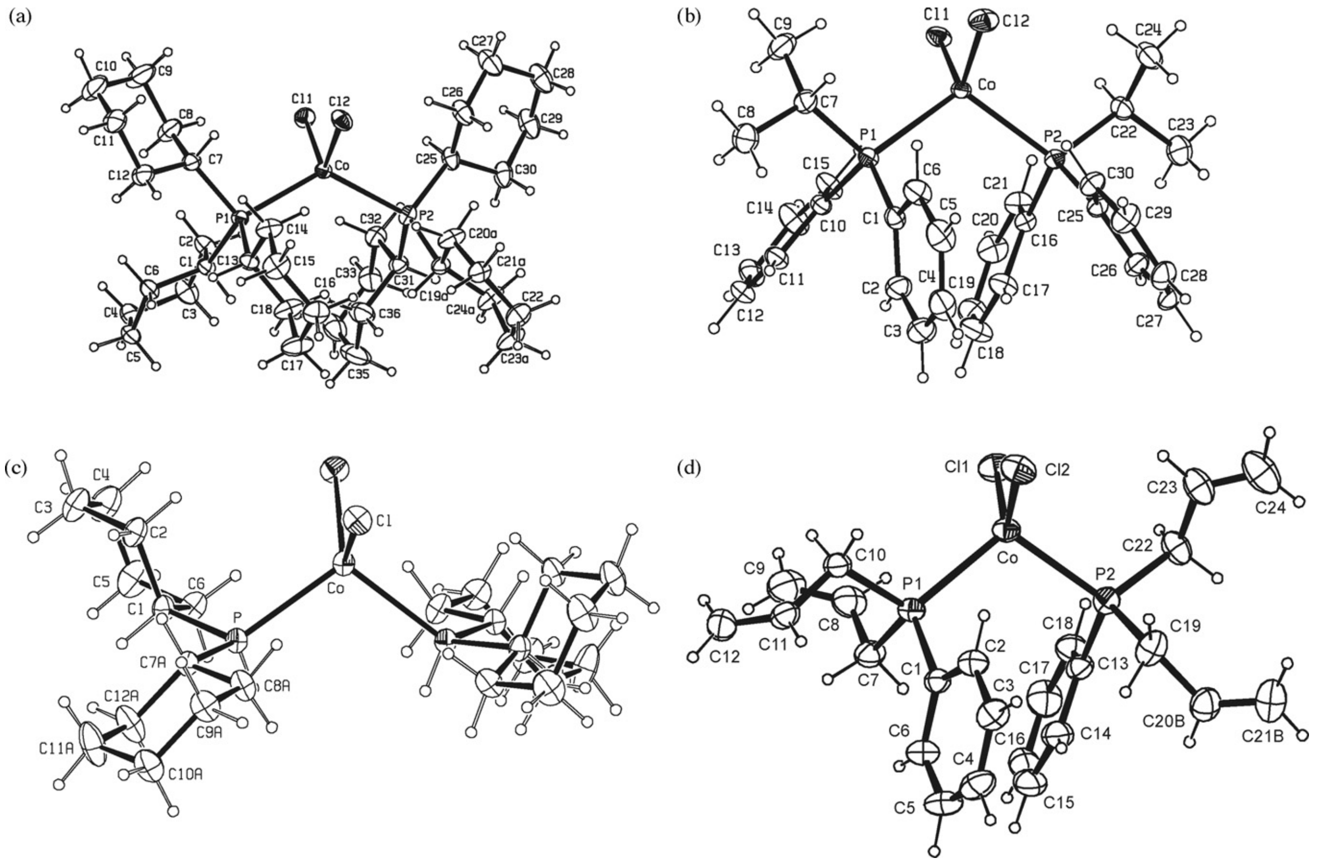

Fig. 16. X-ray crystal structure of (a) $CoCl_2(PCy_3)_2$; (b) $CoCl_2(P^iPrPh_2)_2$; (c) $CoCl_2(PCy_2H)_2$; (d) $CoCl_2(P(C_3H_5)_2Ph)_2$ [71–73].

Table 7
Polymerization of 1,3-butadiene with cobalt catalysts [71–73,75].

Co compound	Polymerization[a]			Polymer microstructure			M_w[e] (g mol^{-1})	M_w/M_n[e]
	Time (min)	Conv. (%)	N[b] (min^{-1})	*cis*-1,4[c] (%)	1,2[c] (%)	*rr*/*mr*/*mm*[d] (molar fraction)		
$CoCl_2$	52	68.6	68	95.4	4.6		815,000	2.2
$CoCl_2(PEt_3)_2$	30	74.8	129	39.9	60.1			
$CoCl_2(P^nPr_3)_2$	35	85.5	127	38.2	61.8			
$CoCl_2(PCy_2H)_2$	30	70.8	122	51.0	49.0		280,000	1.9
$CoCl_2(P^tBu_2H)_2$	35	60.4	89	59.0	41.0		275,000	2.0
$CoCl_2(P^tBu_2Me)_2$	40	59.0	76	94.0	6.0		260,000	1.8
$CoCl_2(PCyp_3)_2$	39	56.4	85	73.6	26.4		245,000	2.0
$CoCl_2(PCy_3)_2$	32	44.4	72	77.4	22.6		250,000	2.1
$CoCl_2(P^iPr_3)_2$	20	57.4	149	94.5	5.5		340,000	2.3
$CoCl_2(P^tBu_3)_2$	22	73.0	172	96.0	4.0		360,000	2.0
$CoCl_2(PMePh_2)_2$	5	64.7	671	23.9	76.1	24/52/24		
$CoCl_2(PEtPh_2)_2$	5	93.7	972	22.3	77.7	42/45/13		
$CoCl_2(P^nPrPh_2)_2$	5	100		21.3	78.7	44/43/13		
$CoCl_2(P^iPrPh_2)_2$	5	100		14.6	85.4	74/26/0		
$CoCl_2(PCyPh_2)_2$	5	75.0	778	15.5	84.5	69/27/4		
$CoCl_2(PMe_2Ph)_2$	5	39.8	413	27.0	73.0	15/51/34		
$CoCl_2(PEt_2Ph)_2$	5	55.4	575	24.7	75.3	19/49/32		
$CoCl_2(PCy_2Ph)_2$	5	55.1	572	20.6	79.4	44/41/15		
$CoCl_2$(dmpm)	86	32.0		95.0	5.0		463,000	2.7
$CoCl_2$(dmpe)	91	55.0		95.2	4.8		237,000	2.6
$CoCl_2$(depe)	76	63.0		94.1	5.9		249,000	2.0
$CoCl_2$(dppe)	125	48.0		96.1	3.9		147,000	2.3
$CoCl_2$(dppp)	100	50.0		96.3	3.7		155,000	2.4

[a] *Polymerization conditions*: butadiene, 2 mL (5 mL in runs 19–23); toluene, total volume 16 mL (40 mL in runs 19–23); MAO, Al/Co = 1000 (Al/Co = 100 in runs 11–18); 5×10^{-6} mol of Co (1×10^{-5} mol in runs 19–23); +20 °C.

[b] N = moles of butadiene polymerized per mol of Co per minute.

[c] Determined by ^{1}H NMR analysis.

[d] Percentages of syndiotactic, atactic and isotactic dyads in the predominantly 1,2-polybutadienes, determined by ^{13}C NMR analysis.

[e] Molecular weight and molecular weight distribution, determined by GPC analysis.

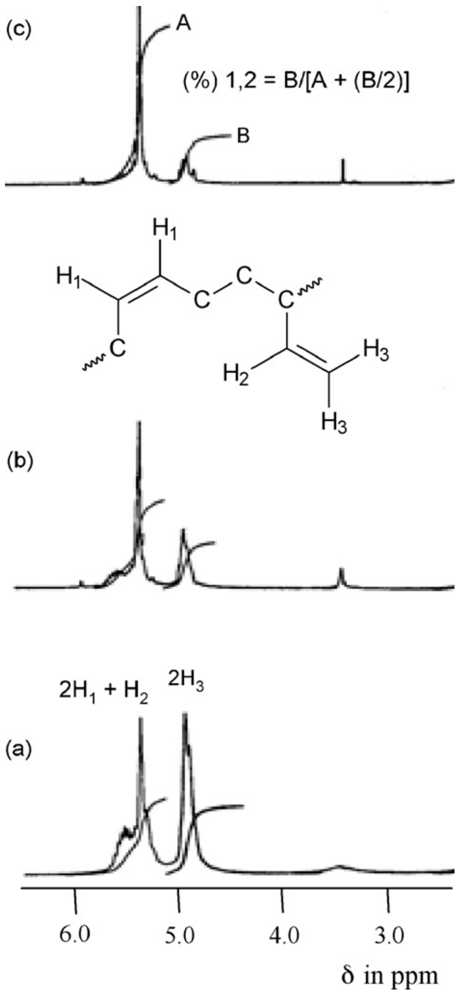

Fig. 17. ^1H NMR spectra ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of polybutadienes obtained with (a) $CoCl_2(P^nPr_3)_2$–MAO; (b) $CoCl_2(^tBu_2H)_2$–MAO; (c) $CoCl_2(PCyp_3)_2$–MAO [71].

were essentially 1,2. The polymer tacticity was strongly dependent on the type of phosphine bonded to the cobalt atom; predominantly syndiotactic polymers were obtained with catalysts with hindered phosphine ligands (*i.e.* P^iPrPh_2, $PCyPh_2$), while atactic polymers were obtained with catalysts with minimally hindered ligands (*i.e.* $PMePh_2$; $PEtPh_2$; P^nPrPh_2) (Fig. 20).

The formation of 1,2-polymers having different tacticity depending on the type of phosphine ligand was interpreted, according to the diene polymerization mechanism proposed by Porri [1,75,86,97,106], by admitting that the incoming butadiene monomer and the allylic unit of the growing polymer chain can assume the two different orientations shown in Fig. 21(a).

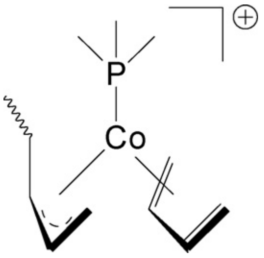

Fig. 18. Active site structure in the polymerization of 1,3-butadiene with cobalt catalysts (only the *exo–exo* structure is shown).

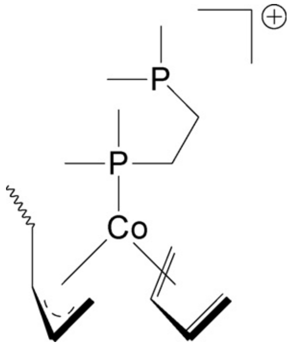

Fig. 19. Possible active site in the polymerization of 1,3-butadiene with $CoCl_2(R_2P(CH_2)_2PR_2)$-based catalysts.

Depending on the type of phosphine ligand, the *exo–exo* or the *exo–endo* orientation can be favored and syndiotactic or isotactic sequences can be formed, respectively; when the steric demand of the ligand is higher (*e.g.* P^iPrPh_2, $PCyPh_2$), the *exo–exo* orientation is the favored one and predominantly syndiotactic polymers are obtained. When the steric demand is lower ($PMePh_2$; $PEtPh_2$; P^nPrPh_2), the *exo–endo* orientation is also possible, isotactic dyads can also be formed, and atactic polymers are obtained.

The polymerization of 1,3-butadiene with the systems $CoCl_2(PR_2Ph)_2$–MAO was also investigated [69,73,75]. The behavior of these systems was very similar to that of the systems $CoCl_2(PRPh_2)_2$–MAO, even if they were characterized by a lower activity and stereospecificity.

5.5. Polymerization of substituted butadienes with $CoCl_2(PRPh_2)_2$–MAO

The polymerization of substituted butadienes such as 1,3-pentadiene, 1,3-hexadiene and 3-methyl-1,3-pentadiene was also studied (Table 8) [72,75,77,78,81].

The systems $CoCl_2(PRPh_2)_2$–MAO (R = methyl, ethyl, *normal*-propyl, *iso*-propyl, cyclohexyl) gave 1,2-polymers from all the above monomers (Fig. 22). As occurred in the polymerization of 1,3-butadiene, the polymers from 1,3-pentadiene and 1,3-hexadiene were predominantly syndiotactic when R = *iso*-propyl or cyclohexyl, while they had an atactic structure, with predominance of syndiotactic sequences, when R = methyl, ethyl or *normal*-propyl. The polymers from 3-methyl-1,3-pentadiene were also crystalline, but exhibited an opposite tacticity, isotactic instead of syndiotactic. In particular $CoCl_2(P^nPrPh_2)_2$–MAO, giving the “less syndiotactic” polybutadienes, polypentadienes, and polyhexadienes, gave the “most isotactic” poly(3-methylpentadiene)s; *vice versa*, $CoCl_2(P^iPrPh_2)_2$–MAO, giving the “most syndiotactic” polybutadiene, polypentadiene, and polyhexadiene, gave the “less isotactic” poly(3-methylpentadiene).

The syndiotactic 1,2-poly(*E*-1,3-pentadiene) [77], syndiotactic 1,2-poly(*E*-1,3-hexadiene) [78] and isotactic 1,2-poly(*E*-3-methyl-1,3-pentadiene) [81] are all novel polymers; all the other systems known failed to give such stereoregular polymers from the above substituted butadienes. The structural characterization of these three crystalline polymers has recently been reported [77,78,81].

The different behavior exhibited by 3-methyl-1,3-pentadiene with respect to the other monomers had some mechanistic implications, and allowed one to clearly highlight for the first time the influence of monomer structure on polymerization stereoselectivity.

Upon the same polymerization catalyst, the formation of 1,2-syndiotactic polymers from *E*-1,3-pentadiene and 1,3-hexadiene, and of 1,2 isotactic polymers from 3-methyl-1,3-pentadiene was explained according to the diene polymerization mechanism. In the

Table 8
Polymerization of 1,3-dienes with $CoCl_2(PRPh_2)_2$–MAO (R = ^{n}Pr, ^{i}Pr)[a] [72,75,77,78,81].

Monomer	Co compound	Time (min)	Conv. (%)	1,2[b] (%)	*rr*[c] (%)	*mm*[c] (%)	M_w[d] ($g\,mol^{-1}$)	M_w/M_n[d]	m.p.[e] (°C)
EP	$CoCl_2(P^iPrPh_2)_2$	180	78.0	≥99	72		220,000	1.7	132
EP	$CoCl_2(P^nPrPh_2)_2$	30	97.2	≥99	45		101,000	1.4	
H	$CoCl_2(P^iPrPh_2)_2$	300	49.9	≥99	63		74,000	1.9	95
H	$CoCl_2(P^nPrPh_2)_2$	300	50.4	≥99	38		65,000	1.7	
3MP	$CoCl_2(P^iPrPh_2)_2$	7200	79.1	≥99		≥60	62,000	1.6	79
3MP	$CoCl_2(P^nPrPh_2)_2$	7200	78.0	≥99		≥90	81,000	1.2	101

[a] *Polymerization conditions*: monomer, 2 ml; toluene, total volume 16 ml; Co, 1×10^{-5} mol; MAO, Al/Co = 100; +20 °C.
[b] Percentage of 1,2 units, determined by ^{1}H NMR analysis.
[c] Triads percentage determined by NMR analysis; complementary percentages are mainly due to *mr* triads.
[d] Molecular weight and molecular weight distribution, determined by GPC analysis.
[e] Melting point, determined by DSC analysis.

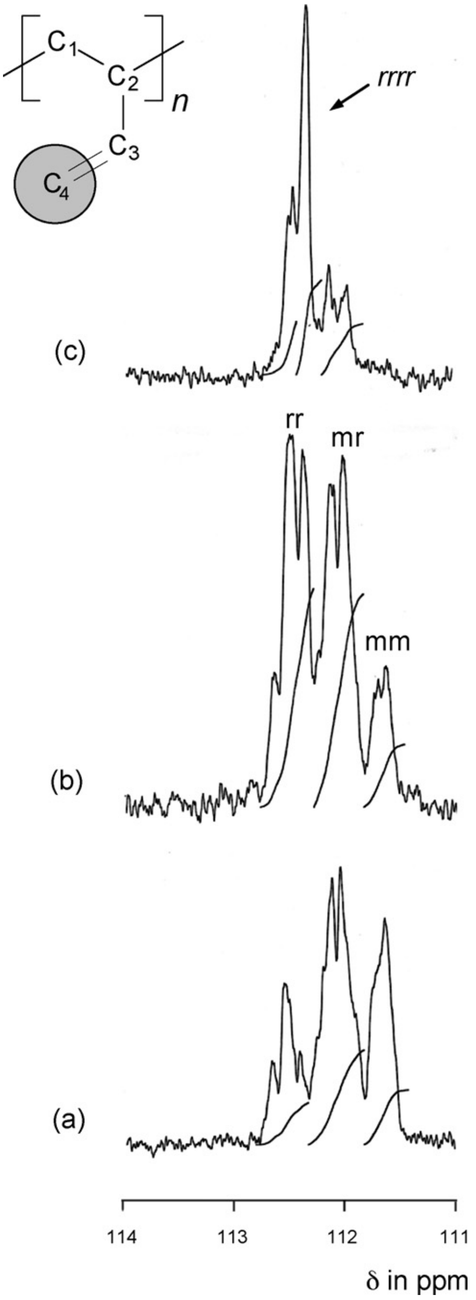

Fig. 20. ^{13}C NMR spectra ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C; olefinic region, C4 signal) of 1,2-polybutadienes obtained with (a) $CoCl_2(PMePh_2)_2$–MAO; (b) $CoCl_2(P^nPrPh_2)_2$–MAO; (c) $CoCl_2(P^iPrPh_2)_2$–MAO [72,73].

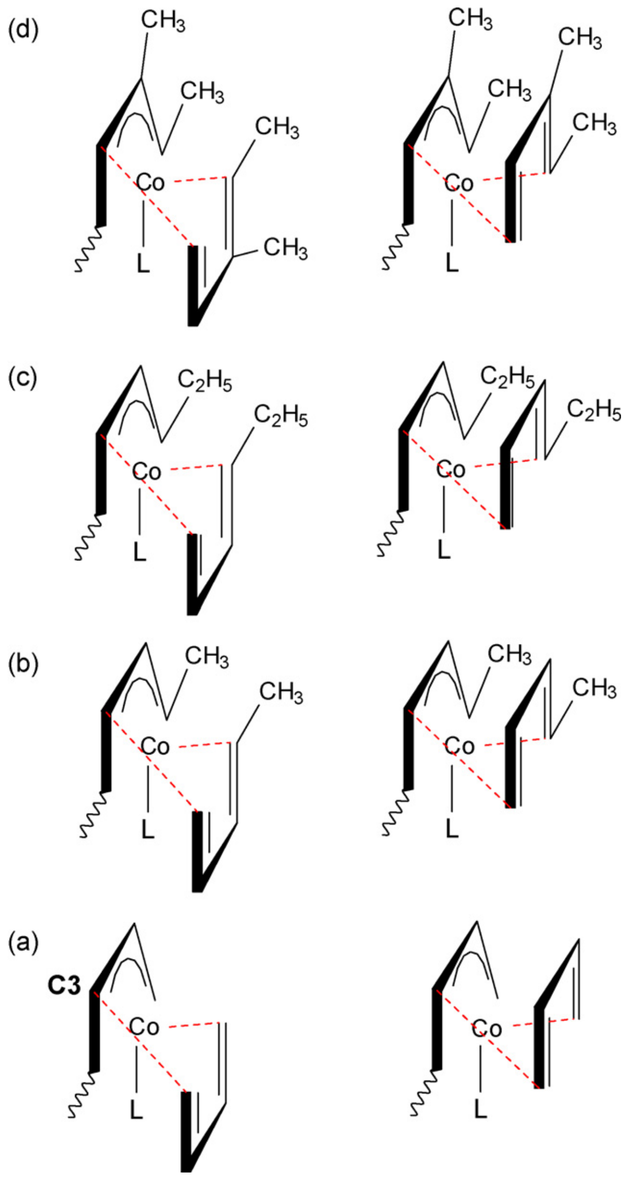

Fig. 21. Diene-butenyl group orientations in the polymerization of (a) 1,3-butadiene, (b) 1,3-pentadiene, (c) 1,3-hexadiene, (d) 3-methyl-1,3-pentadiene to 1,2-polymers with $CoCl_2(PRPh_2)_2$–MAO (*exo–endo* structure on the left; *exo–exo* structure on the right).

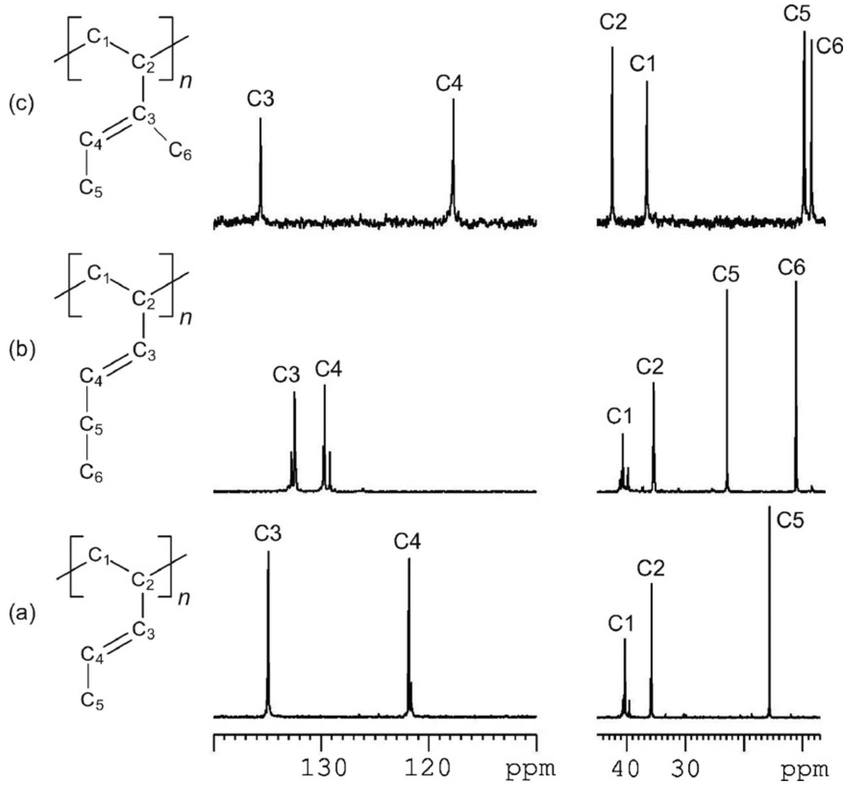

Fig. 22. ^{13}C NMR spectra ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of (a) syndiotactic 1,2-poly(*E*-1,3-pentadiene) obtained with $CoCl_2(P^iPrPh_2)_2$–MAO; (b) syndiotactic 1,2-poly(*E*-1,3-hexadiene) obtained with $CoCl_2(P^iPrPh_2)_2$–MAO; (c) isotactic 1,2-poly(*E*-3-methyl-1,3-pentadiene) obtained with $CoCl_2(P^nPrPh_2)_2$–MAO [77,78,81].

case of *E*-1,3-pentadiene (Fig. 21(b)) and 1,3-hexadiene (Fig. 21(c)), the favored incoming monomer-butadienyl group orientation is the *exo–exo* one, while in the case of 3-methyl-1,3-pentadiene (Fig. 21(d)) the preferred orientation is the *exo–endo* one. In fact, in the case of the *exo–endo* orientation, the insertion of the incoming monomer at C3 of the butadienyl group affords a 1,2 isotactic dyad, while a 1,2-syndiotactic dyad is obtained in the case of the *exo–exo* orientation. Most probably in the polymerization of internal substituted dienes such as 3-methyl-1,3-pentadiene, the steric hindrance due to the presence of a methyl on the C2 carbon of the butadienyl group and on the C3 carbon of the incoming monomer forces the two groups to assume an *exo–endo* orientation, even if it is not the favored one when a ligand (less or more hindered) is bonded to the metal.

5.6. Polymerization of butadiene with cobalt complexes with nitrogen ligands

Some papers concerning the polymerization of 1,3-butadiene with catalysts based on cobalt complexes with nitrogen ligands have been reported [139,144,145], but an in-depth investigation on the influence of the ligand nature on chemo- and stereoselectivity has not been carried out.

Co(II)-based pyridylbis(imine) complexes combined with ethylaluminum sesquichloride (EASC) as cocatalyst showed good activity in butadiene polymerization giving *cis*-1,4-polymers up to about 96%. Highly syndiotactic 1,2-polybutadiene was obtained with a halogen-free pyridine cobalt complex and trialkylaluminum or a mixture of trialkylaluminum and dialkylaluminum halide.

6. Nickel catalysts

A wide variety of nickel-based catalysts has been reported in the literature as active in butadiene polymerization [145–149]. Specifically, the catalyst system $AlEt_3$–Ni(octanoate)$_2$–$BF_3\cdot OEt_2$ is currently used for the industrial production of high *cis*-polybutadiene (*cis* content 96–97%).

A few papers have also reported on the polymerization of butadiene with catalysts based on well-defined nickel complexes with phosphorus and nitrogen ligands. Ni(II)-based pyridylbis(imine) complexes combined with ethylaluminum sesquichloride (EASC) as cocatalyst showed good activity in butadiene polymerization affording *cis*-1,4-polymers up to about 95% [150]. A cationic allylnickel complex stabilized by a single N-heterocyclic carbene ligand and a labile acquo ligand was moderately active for the polymerization of 1,3-butadiene (*cis*-1,4, 92%) [151]. The dicationic nickel complex $[(dppf)Ni(MeCN)_4][BF_4]_2$ in combination with $AlEt_2Cl$ exhibited high activity in the butadiene polymerization. The resulting polybutadiene showed surprisingly high *cis*-1,4 content (>80%) and only 2% of 1,2 units. In fact in the presence of phosphorus ligands the polymerization produces a polymer with high *trans*-1,4 units. The polymers obtained presented low molecular weights [152].

Several papers deal with the polymerization of butadiene with allyl nickel complexes [153–155]. Ni(bipy)Et$_2$ cyclooligomerized butadiene to cyclododecatriene [127]. The bis(triphenylphosphine)(η^3-crotyl)nickel cation was used as catalyst precursor for the oligomerization of butadiene to cyclic or linear dimers. Oligomers were also produced in variable amounts [146,156].

7. Titanium catalysts

Some complexes of Ti(II) and Ti(IV) with bidentate dialkylphosphines (*e.g.* $TiCl_2(dmpe)_2$; $TiCl_4(dmpe)_2$; $TiCl_4(depe)_2$) [109,157,158] were used in combination with MAO for the polymerization of 1,3-butadiene (Table 9) [158]. The systems thus obtained had a rather low activity and stereospecificity, giving polymers with a mixed *cis*-1,4/1,2 structure.

Table 9
Polymerization of 1,3-butadiene with titanium catalysts.[a].

Ti compound	Conv. (%)	Polymer microstructure[b]		
		cis-1,4 (%)	*trans*-1,4 (%)	1,2 (%)
$TiCl_4$(dmpm)	8.7	78.0	6.0	16.0
$TiCl_4$(dmpe)	11.9	80.0	2.9	17.1
$TiCl_4$(depe)	29.6	81.6	4.3	14.1
$TiCl_4$(dppm)	10.6	75.6	7.6	16.9
$TiCl_4$(dppe)	27.4	79.2	5.6	15.2

[a] *Polymerization conditions*: butadiene, 2 mL; toluene, total volume 16 mL; Al/Ti = 1000; 1×10^{-5} mol of Ti; +20 °C; 180 min.
[b] Determined by IR analysis.

Pellecchia et al. reported that the catalytic system obtained by combining a bis(phenoxyimino)titanium dichloride with MAO is able to polymerize 1,3-dienes to predominantly *cis*-1,4-polymers with a good activity [159].

8. Conclusions

The impressive advancement achieved in olefin polymerization with the introduction of catalysts based on well-defined transition metal complexes has been only partially mirrored, until now, by similar progress in diene polymerization. In the latter field, the catalytic activity of several metals has not yet been adequately explored and, even for the more studied metals, only few metal/ligand couples have been evaluated.

Nevertheless, several Cr, Fe, or Co complexes with phosphines or with nitrogen ligands are very active catalysts, even in aliphatic hydrocarbon media, showing, at the same time, high chemo- and stereoselectivity. They permit one to obtain butadiene polymers with controlled microstructure and with a quite narrow molecular weight distribution ($M_w/M_n \leq 2$), suggesting a single-site catalyst nature. The use of these novel catalyst systems might allow the production of new polybutadienes for novel applications.

These new systems are also able to polymerize different types of substituted butadienes, giving polymers with different structure from different monomers. Specifically, they allowed one to synthesize several novel stereoregular polydienes which could not be prepared with other catalytic systems.

Thanks to their ability to polymerize different types of monomers, it was possible to obtain considerable information useful for a better comprehension of the diene polymerization mechanism. They permitted, on one hand, to confirm and support some aspects of the well-known polymerization mechanism proposed several years ago by Porri (*i.e.* the influence of catalyst structure on the polymerization chemo- and stereoselectivity and of the monomer structure on the polymerization chemoselectivity) and, on the other hand, to clearly point out for the first time the fundamental role played by monomer structure in determining the polymerization stereoselectivity. Thus, the system $CrCl_2(dmpe)_2$–MAO gives a 1,2-syndiotactic polymer from butadiene, but a 3,4-polymer with a predominantly isotactic structure from isoprene; the system $CoCl_2(P^{i}PrPh_2)_2$–MAO gives a highly syndiotactic 1,2-polymer from 1,3-pentadiene, but a 1,2 isotactic polymer from 3-methyl-1,3-pentadiene.

The same monomer, however, does not exhibit the same behavior with all the catalysts. Isoprene gives a 3,4-polymer with a predominantly isotactic structure when polymerized with $CrCl_2(dmpe)_2$–MAO, but a highly syndiotactic 3,4-polymer when polymerized with $FeCl_2(bipy)_2$–MAO; 3-methyl-1,3-pentadiene gives a highly isotactic 1,2-polymer when polymerized with $CoCl_2(PMePh_2)_2$–MAO, but a highly syndiotactic 1,2-polymer when polymerized with $FeCl_2(bipy)_2$–MAO.

The above experimental evidence suggests that the polymerization stereoselectivity, which for 1,3-dienes depends on the reciprocal orientation (*exo–exo* or *exo–endo*) of incoming monomer and butenyl group, is determined by two main factors: catalytic structure (type of transition metal and type of coordinated ligand) and monomer structure (presence of alkyl substituents on the different carbons of the monomeric unit).

A highly 1,2-syndiotactic polydiene is obtained when both factors are in favor of an *exo–exo* orientation of incoming diene monomer and butenyl group of the growing polymer chain, *i.e.* hindered ligand and terminally substituted diene; a highly 1,2 isotactic polydiene is instead obtained if the two factors are in favor of an *exo–endo–endo* orientation, *i.e.* minimally hindered ligand and internally substituted diene. For all the other combinations (*i.e.* bulky ligand and internally substituted monomer; minimally hindered ligand and terminally substituted monomer) 1,2 atactic polymers, with predominance of isotactic or syndiotactic sequences, can be formed.

The aforementioned hypotheses are supported by the results obtained in the polymerization of butadiene and isoprene with $CrCl_2(dmpe)_2$–MAO, and in the polymerization of butadiene and 3-methyl-1,3-pentadiene with $FeEt_2(bipy)_2$–MAO.

The system $CrCl_2(dmpe)_2$–MAO gives a highly syndiotactic 1,2-polymer from butadiene but an atactic 3,4-polymer from isoprene (internally substituted butadiene). This experimental observation can be interpreted by assuming that in the case of isoprene polymerization the ligand is not bulky enough to completely cancel the effect of the monomer structure, which is in favor of an *exo–endo* orientation; both *exo–exo* and *exo–endo* orientations are possible and atactic polymers are indeed formed.

The system $FeEt_2(bipy)_2$–MAO gives 1,2-syndiotactic polymers from both butadiene and 3-methyl-1,3-pentadiene. The interpretation given is that in the case of 3-methyl-1,3-pentadiene (internally substituted butadiene) the ligand bulkiness is such as to dominate the effect of the monomer structure, which would be in favor of an *exo–endo* orientation, and highly syndiotactic polymer is obtained also from 3-methyl-1,3-pentadiene.

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