

Synthesis, structure and butadiene polymerization behavior of $\text{CoCl}_2(\text{PR}_x\text{Ph}_{3-x})_2$ (R = methyl, ethyl, propyl, allyl, isopropyl, cyclohexyl; x = 1, 2). Influence of the phosphorous ligand on polymerization stereoselectivity

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Dedicated to the memory of Roberto Santi, who was an irreplaceable teacher and friend for all of us

Abstract

Several cobalt(II) phosphine complexes have been synthesized by reacting cobalt(II) chloride with various mono- and diphenylalkylphosphines ($\text{PR}_x\text{Ph}_{3-x}$; R = methyl, ethyl, allyl, propyl, isopropyl, cyclohexyl; x = 1, 2). For some of these complexes single crystals were obtained and their molecular structures were determined by X-ray diffraction method. All the complexes were then used in association with MAO for the polymerization of 1,3-butadiene and they were found to be extremely active. Predominantly 1,2 polymers having different tacticity (predominantly iso- or syndiotactic), depending on the type of phosphine ligand bonded to the cobalt atom, were obtained. An interpretation of this particular behavior, based on the diene polymerization mechanism previously proposed, is reported.

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1. Introduction

We have recently found that the systems $\text{CoCl}_2(\text{PR}_3)_2$ –MAO (R = alkyl group) give, from butadiene, polymers with different structure (*cis*-1,4; mixed *cis*-1,4/1,2; predominantly 1,2) depending on the type of phosphine ligand [1], meaning that the ligand has a strong influence on the polymerization chemoselectivity.

Predominantly 1,2 polybutadienes having an atactic structure were obtained with systems using less hindered phosphines (e.g., PEt_3 , P^iPr_3), while essentially *cis*-1,4 polybutadienes were prepared by using more hindered phosphines (e.g., $\text{P}^t\text{Bu}_2\text{Me}$). We have also reported on the synthesis of $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ and its behavior in the polymerization of butadiene [2]; when used in association with MAO, it was found to be extremely active and stereospecific, giving a highly syndiotactic 1,2 polybutadiene. If we consider that, as cited above, the system $\text{CoCl}_2(\text{PEt}_3)_2$ –MAO gives from butadiene a

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predominantly 1,2 polymer having an atactic structure, it follows that the type of phosphorous ligand may influence the polymerization stereoselectivity, too.

We thought to check this experimental indication by synthesizing some new cobalt complexes using different mono- and diphenylalkyl phosphines [3] (PMePh_2 ,

PMe_2Ph , PEtPh_2 , PEt_2Ph , P(allyl)Ph_2 , $\text{P(allyl)}_2\text{Ph}$, P^nPrPh_2 , PCyPh_2 , PCy_2Ph ; Me = methyl, Et = ethyl, ^nPr = *normal*-propyl, Cy = cyclohexyl) in which the steric demand of the alkyl group is varied with respect to $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$: it is well known that steric and electronic properties of the phosphines are strongly influenced by the nature of substituents on the

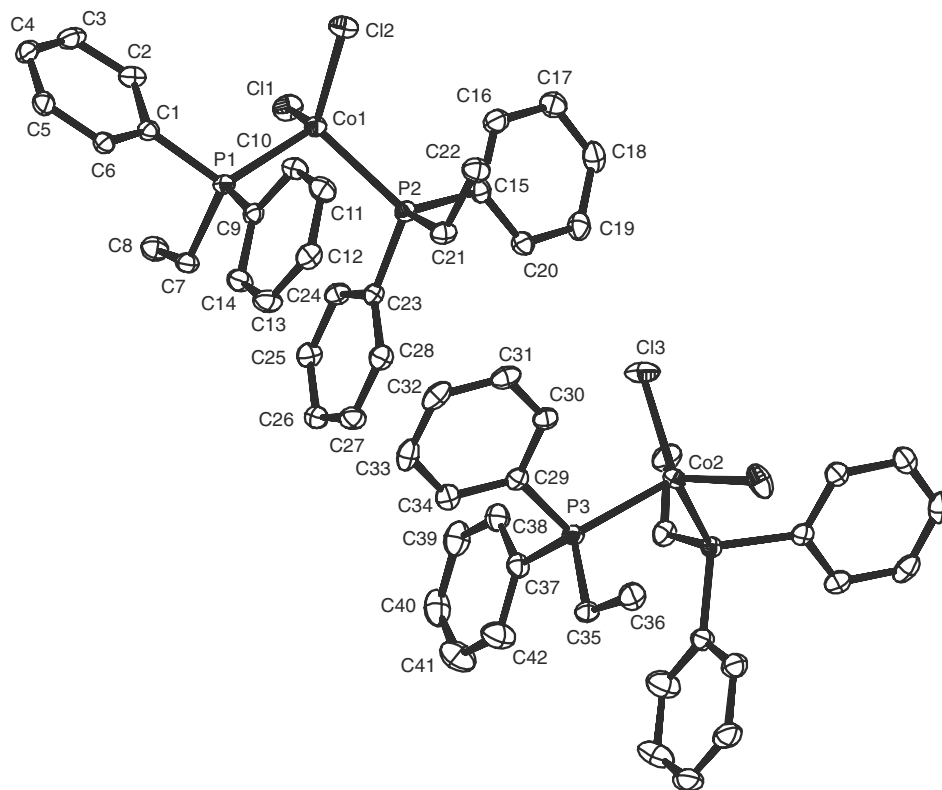


Fig. 1. ORTEP plot of $\text{CoCl}_2(\text{PEtPh}_2)_2$ [13] with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability. Hydrogen atoms are omitted for clarity.

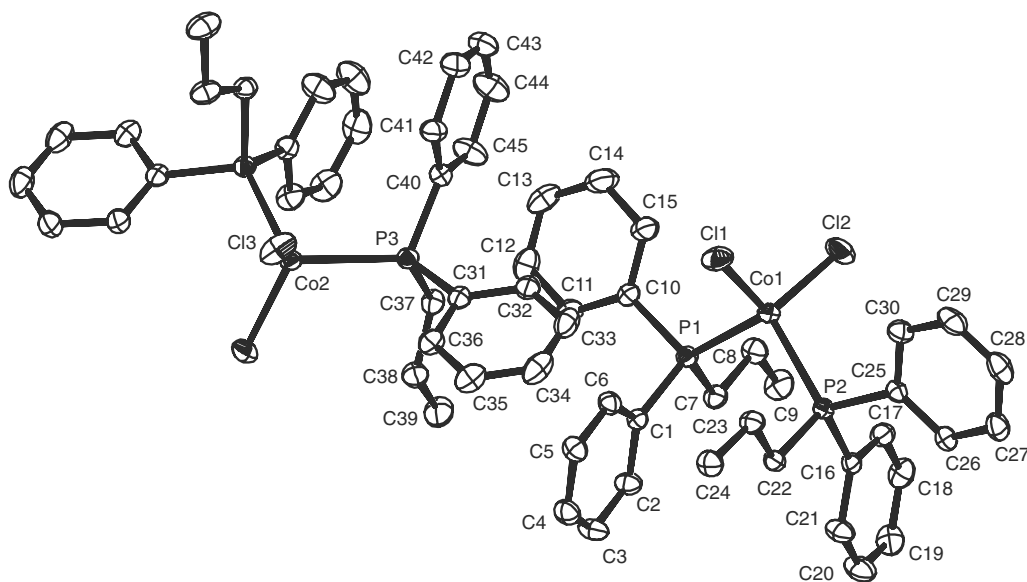


Fig. 2. ORTEP plot of $\text{CoCl}_2(\text{P}^n\text{PrPh}_2)_2$ [13] with atom numbering scheme. Displacement ellipsoids are drawn at the 20% probability. Hydrogen atoms are omitted for clarity.

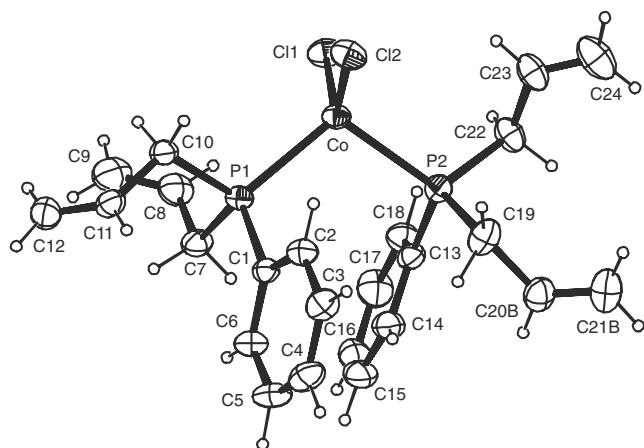


Fig. 3. ORTEP plot of $\text{CoCl}_2(\text{P}(\text{allyl})_2\text{Ph})_2$ [13] with atom numbering scheme. Displacement ellipsoids are drawn at the 20% probability.

Table 1
Selected bond lengths (Å) and angles (°) for $\text{CoCl}_2(\text{PEtPh}_2)_2$

Co1–Cl1	2.2276(7)
Co1–Cl2	2.2201(7)
Co2–Cl3	2.2145(6)
Co1–P1	2.3747(6)
Co1–P2	2.3760(6)
Co2–P3	2.3654(6)
P1–C1	1.8134(18)
P1–C7	1.8304(19)
P1–C9	1.8179(18)
P2–C15	1.8097(19)
P2–C21	1.8319(19)
P2–C23	1.8131(19)
P3–C29	1.8173(18)
P3–C35	1.8262(19)
P3–C37	1.8127(19)
Cl1–Co1–Cl2	110.57(2)
Cl3–Co2–Cl3'	115.07(4)
P1–Co1–P2	100.63(2)
P3–Co2–P3'	105.15(3)
Cl1–Co1–P1	111.85(2)
Cl1–Co1–P2	109.92(2)
Cl2–Co1–P1	111.01(2)
Cl2–Co1–P2	112.52(2)
Cl3–Co2–P3	106.94(2)
Cl3–Co2–P3'	111.17(2)
C1–P1–C7	103.22(8)
C1–P1–C9	105.85(8)
C7–P1–C9	104.37(8)
C15–P2–C21	104.69(9)
C15–P2–C23	104.87(8)
C21–P2–C23	104.22(8)
C29–P3–C35	104.00(9)
C29–P3–C37	105.11(8)
C35–P3–C37	104.67(9)

phosphorous atom [4]. The crystalline structures of some of these complexes were determined and then they were used in combination with MAO for the polymerization of 1,3-butadiene [5]. The results obtained are reported in the present paper.

Table 2
Selected bond lengths (Å) and angles (°) for $\text{CoCl}_2(\text{P}^n\text{PrPh}_2)_2$

Co1–Cl1	2.2118(9)
Co1–Cl2	2.1960(9)
Co2–Cl3	2.2090(8)
Co1–P1	2.3691(8)
Co1–P2	2.3640(10)
Co2–P3	2.3940(9)
P1–C1	1.811(2)
P1–C7	1.827(2)
P1–C10	1.815(3)
P2–C16	1.814(2)
P2–C22	1.826(2)
P2–C25	1.816(2)
P3–C31	1.820(3)
P3–C37	1.827(2)
P3–C40	1.810(3)
Cl1–Co1–Cl2	112.60(3)
Cl3–Co2–Cl3'	113.49(6)
P1–Co1–P2	103.73(3)
P3–Co2–P3'	105.97(4)
Cl1–Co1–P1	108.36(4)
Cl1–Co1–P2	111.46(4)
Cl2–Co1–P1	111.11(3)
Cl2–Co1–P2	109.23(3)
Cl3–Co2–P3	107.82(3)
Cl3–Co2–P3'	110.75(3)
C1–P1–C7	105.16(11)
C1–P1–C10	105.98(11)
C7–P1–C10	103.12(12)
C16–P2–C22	106.24(11)
C16–P2–C25	105.73(11)
C22–P2–C25	102.02(11)
C31–P3–C37	102.32(11)
C31–P3–C40	105.27(12)
C37–P3–C40	105.04(12)

Table 3
Selected bond lengths (Å) and angles (°) for $\text{CoCl}_2(\text{P}(\text{allyl})_2\text{Ph})_2$

Co–Cl1	2.2095(7)
Co–Cl2	2.2092(7)
Co–P1	2.3565(7)
Co–P2	2.3490(7)
P1–C1	1.816(2)
P1–C7	1.826(2)
P1–C10	1.839(2)
P2–C13	1.810(2)
P2–C19	1.831(2)
P2–C22	1.826(2)
Cl1–Co–Cl2	117.29(3)
P1–Co–P2	106.58(2)
Cl1–Co–P1	114.46(2)
Cl1–Co–P2	100.28(2)
Cl2–Co–P1	104.59(2)
Cl2–Co–P2	113.43(2)
C1–P1–C10	103.75(9)
C1–P1–C7	105.63(9)
C10–P1–C7	104.86(10)
C13–P2–C22	105.97(9)
C13–P2–C19	106.82(11)
C22–P2–C19	104.76(11)

2. Results and discussion

2.1. Synthesis and characterization of cobalt complexes

The complexes were prepared following a general experimental procedure already reported in the literature [6]. CoCl_2 was reacted with an excess of phosphine using ethanol as solvent. Crystalline products were obtained by continuous extraction of the reaction products with boiling pentane or toluene. Single crystals were obtained in the case of $\text{CoCl}_2(\text{PEtPh}_2)_2$, $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ and $\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$, and their structures determined by X-ray diffraction. For $\text{CoCl}_2(\text{PMePh}_2)_2$ and $\text{CoCl}_2(\text{PCyPh}_2)_2$, structure determination was not possible owing to large disorder affecting both structures. No monocrystals have been obtained for all the other complexes.

The molecular structures of $\text{CoCl}_2(\text{PEtPh}_2)_2$, $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ and $\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$ are shown in Figs. 1–3, respectively, and selected bond lengths and angles are reported in Tables 1–3. The complexes show a distorted tetrahedral coordination around the Co(II)

centre. The largest deviations from the ideal tetrahedral geometry, $117.29(3)^\circ$ and $100.28(2)^\circ$, are observed in $\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$ for the angles Cl1-Co-Cl2 and Cl1-Co-P2 , respectively. In all cases, the Cl-Co-Cl angles are found systematically larger than the tetrahedral value, while the opposite trend is observed for the P-Co-P angles.

The crystal structures of $\text{CoCl}_2(\text{PEtPh}_2)_2$ and $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ are very similar, as it appears by comparing not only the geometrical parameters of Tables 1 and 2, but also the structural data reported in Table 4. In both cases the space group is $C2/c$, with one and a half molecules in the asymmetric unit and a very long (up to 47 \AA) a cell side. By averaging on all the chemically equivalent bond lengths, the values $\text{Co-Cl} = 2.221$ and 2.206 \AA , $\text{Co-P} = 2.372$ and 2.376 \AA , $\text{P-C}_{\text{aromatic}} = 1.814 \text{ \AA}$ (in both structures), $\text{P-C}_{\text{aliphatic}} = 1.830$ and 1.827 \AA are obtained in $\text{CoCl}_2(\text{PEtPh}_2)_2$ and $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$, respectively. When comparing these two systems with the previously studied $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ complex, [2] we observe only slight differences, the larger one being a longer $\text{P-C}_{\text{aliphatic}}$ average distance (1.850 \AA)

Table 4

Crystal data, details of data collection and results of the refinement for $\text{CoCl}_2(\text{PEtPh}_2)_2$, $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ and $\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$

Compound	$\text{CoCl}_2(\text{PEtPh}_2)_2$	$\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$	$\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$
Formula	$\text{C}_{28}\text{H}_{30}\text{Cl}_2\text{CoP}_2$	$\text{C}_{30}\text{H}_{34}\text{Cl}_2\text{CoP}_2$	$\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{CoP}_2$
M_r	558.29	586.34	510.25
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$
Z	12	12	2
D_{calc} (g cm^{-3})	1.400	1.331	1.292
Unit cell dimensions			
a (\AA)	46.361(9)	47.058(9)	9.377(2)
b (\AA)	9.863(2)	10.169(2)	10.336(2)
c (\AA)	18.645(4)	19.538(4)	13.654(3)
α ($^\circ$)	90	90	87.235(10)
β ($^\circ$)	111.28(1)	110.12(3)	86.248(10)
γ ($^\circ$)	90	90	83.913(10)
V (\AA^3)	7944(3)	8779(3)	1312.0(5)
Crystal size (mm)	$0.52 \times 0.32 \times 0.10$	$0.25 \times 0.17 \times 0.10$	$0.30 \times 0.24 \times 0.08$
Color, habit	Light blue, prism	Light blue, prism	Light blue, prism
μ (mm^{-1})	0.986	0.896	0.988
Radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
T (K)	90(2)	293(2)	293(2)
$2\theta_{\text{max}}$ ($^\circ$)	56.5	53.7	66.2
h, k, l ranges	$-61 \rightarrow 60; -12 \rightarrow 12; -24 \rightarrow 24$	$-59 \rightarrow 59; -12 \rightarrow 12; -24 \rightarrow 24$	$-14 \rightarrow 14; -15 \rightarrow 15; -20 \rightarrow 20$
Intensity decay, %	0.00	0.00	0.00
Absorption correction	Multi-scan (Bruker SADABS)	None	Multi-scan (Bruker SADABS)
$T_{\text{min}}, T_{\text{max}}$	0.899, 1.000	–	0.908, 1.000
Number of measured reflections	52 731	53 660	19 647
R_{int}	0.0298	0.0580	0.0257
Number of independent reflections	9433	9060	9105
Number of reflections with $I > 2\sigma(I)$	8701	5619	4753
Number of parameters, restraints	447, 0	474, 0	281, 3
$R(F^2), wR(F^2)$	0.0396, 0.0898	0.0671, 0.0847	0.0884, 0.1146
$R[F^2 > 2\sigma(F^2)], wR[F^2 > 2(F^2)]$	0.0365, 0.0882	0.0375, 0.0799	0.0423, 0.1026
Goodness-of-fit	1.058	0.867	0.897
$(\Delta/\sigma)_{\text{max}}$	0.001	0.001	0.001
$\Delta\rho_{\text{max}}, \rho_{\text{min}}$ (e \AA^{-3})	0.968, -0.397	0.285, -0.217	0.374, -0.194

in $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$, which can be ascribed to the larger bulkiness of the isopropyl group with respect to the ethyl and the *n*-propyl groups.

Complex $\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$ is very similar to the previously discussed ones, as far as the relevant structural parameters are concerned. The only remarkable difference, in agreement with the reduced bulkiness of the phosphine ligands, is observed in the Co–P distances (2.353 Å on average), which are slightly shorter than the corresponding ones in $\text{CoCl}_2(\text{PEtPh}_2)_2$ and $\text{CoCl}_2(\text{P}^n\text{PrPh}_2)_2$.

Analysis of crystal packing reveals the presence of C–H...Cl intermolecular hydrogen bonds in all structures, the stronger ones being C12–H12A...Cl1_{–x,–y,1–z} and C15–H15...Cl2_{1+x,y,z} in complex $\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$ (H...Cl distances 2.80(1) and 2.90(1) Å, C–H...Cl angles 150(1)° and 167(1)°, respectively). Moreover, in $\text{CoCl}_2(\text{PEtPh}_2)_2$ and $\text{CoCl}_2(\text{P}^n\text{PrPh}_2)_2$ the presence of several π – π interactions between phenyl rings arranged in T-shape configuration can be detected on the basis of geometrical considerations. The dihedral angles between the least-square planes through the interacting rings fall in the range 85(1)–90(1)°, and one or two H atom of a phenyl ring point towards the centre or a bond of the other ring. The shortest approaching distance is observed in $\text{CoCl}_2(\text{PEtPh}_2)_2$, where the atom H25_{x,1–y,1/2+z} is placed at 2.54(1) Å from the plane of the ring C29–C34, pointing approximately towards its centre.

2.2. Polymerization of 1,3-butadiene

The results obtained in the polymerization of butadiene with the various cobalt complexes are shown in Table 5 and can be summarized as follows; the results obtained with the system $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ –MAO, already reported in the literature [2], are added for comparison.

- (i) The systems $\text{CoCl}_2(\text{PRPh}_2)_2$ –MAO (R = methyl, *normal*-propyl, ethyl, allyl, *iso*-propyl, cyclohexyl) were found to be extremely active in the polymerization of butadiene; in general complete conversions were reached in a few minutes. The polymers obtained are essentially 1,2, as indicated by their ¹H NMR spectra (Fig. 4); the 1,2 content is in the range 70–88%, and varies with varying the type of catalyst and the polymerization conditions. The remaining units are essentially *cis*-1,4; the band at 967 cm^{–1} in the IR spectra of the polymers, indicative of the presence of *trans*-1,4 units, is almost negligible.
- (ii) The polymer tacticity strongly depends on the type of catalyst, i.e., the type of phosphine bonded to the cobalt atom. The syndiotactic index (expressed as percentage of syndiotactic triads *rr*) of the polymers, determined by their ¹³C NMR spectra (Fig. 5), increases with increasing the hindrance of the phosphorous ligand, i.e., the steric demand

Table 5
Polymerization of butadiene with different cobalt systems^a

Run	Catalyst		Polymerization		Polymer microstructure ^b			m.p. (°C)
	Co-compound	Al/Co (molar ratio)	Time (min)	Conv (%)	<i>cis</i> (%)	1,2 (%)	rr:mr:mm (molar fraction)	
1	$\text{CoCl}_2(\text{PMePh}_2)_2$	1000	5	58.0	29.9	70.1	23/47/30	–
2		500	5	59.2	27	73.0	23/51/26	–
3		100	5	64.7	23.9	76.1	24/52/24	–
4		50	60	26.0	27.0	73.0	24/52/24	–
5		20	60	15.2	26.0	74.0	25/52/23	–
6	$\text{CoCl}_2(\text{PEtPh}_2)_2$	100	5	93.7	22.3	77.7	42/45/13	–
7	$\text{CoCl}_2(\text{P}^n\text{PrPh}_2)_2$	100	5	100	21.3	78.7	44/43/13	–
8	$\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$	100	5	76	19.8	80.2	41/44/15	–
9	$\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$	100	5	100	14.6	85.4	74/26/0	126
10	$\text{CoCl}_2(\text{PCyPh}_2)_2$	1000	5	72	17.3	82.7	71/25/4	117
11 ^c		1000	2	100	12	88.0	76/22/2	132
12		500	5	70.8	20	80.0	68/28/4	106
13		100	5	75.0	15.5	84.5	69/27/4	109
14 ^c		100	3	100	12	88.0	78/20/2	139
15		20	60	33.4	16	84.0	70/27/3	115
16	$\text{CoCl}_2(\text{PMe}_2\text{Ph})_2$	100	5	39.8	27.0	73.0	15/51/34	–
17	$\text{CoCl}_2(\text{PEt}_2\text{Ph})_2$	100	5	55.4	24.7	75.3	19/49/32	–
18	$\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$	100	5	40.1	26.0	74.0	22/49/29	–
19	$\text{CoCl}_2(\text{PCy}_2\text{Ph})_2$	100	5	55.1	20.6	79.4	44/41/15	–

^a Polymerization conditions: butadiene, 2 ml; toluene, total volume 16 ml; MAO; 5×10^{-6} mol of Co (1×10^{-5} mol in runs 4,5 and 15); +20 °C. The molecular weight (MW) and molecular weight distribution (MWD) of the amorphous 1,2 polybutadienes are in the range 250–300000 g/mol and 2–2.5, respectively. The predominantly syndiotactic 1,2 polybutadienes (runs 9–15) were not soluble in the GPC conditions used.

^b Determined by ¹H and ¹³C NMR analysis; *trans*-1,4 units were found to be negligible, as indicated by the extremely low intensity of the band at 967 cm^{–1} in the IR spectra of the polymers.

^c Heptane as solvent was used instead of toluene.

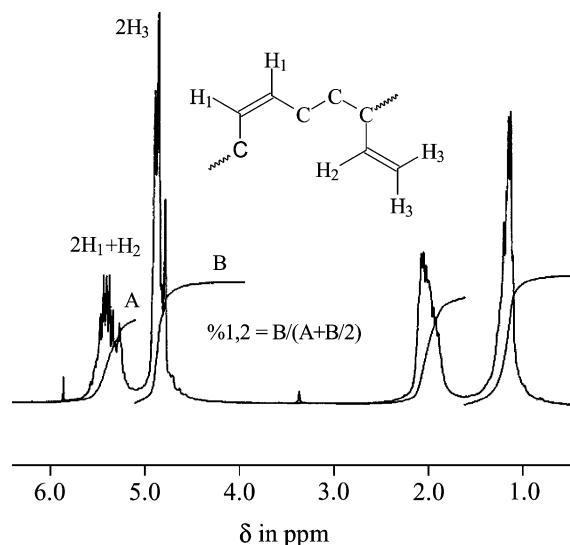


Fig. 4. ^1H NMR spectrum ($\text{C}_2\text{D}_2\text{Cl}_4$, HMDS as internal standard, 103°C) of the polybutadiene obtained with the system $\text{CoCl}_2(\text{P-CyPh}_2)_2\text{-MAO}$ (Table 5, run 13).

of the alkyl group bonded to the phosphorous atom (compare, for instance, runs 3, 6–9, and 13 in Table 5).

- (iii) The 1,2 polybutadienes obtained with the cobalt systems using less hindered ligands (e.g., PMePh_2 ; PEtPh_2 ; P^nPrPh_2) are amorphous and no melting point could be detected; the T_g values of these polymers were found to be in the range -10 to -15°C . The polymers obtained with systems using more hindered ligands (e.g., P^iPrPh_2 and PCyPh_2) are crystalline by X-ray with a melting point ranging from 109 to 139°C , depending on the polymerization conditions. They exhibited T_g values around $3\text{--}5^\circ\text{C}$ and crystallization enthalpies ranging from -10 to -20 J/g .
- (iv) In general the Al/Co molar ratio does not affect the stereospecificity, but it has some influence on the catalyst activity. When the Al/Co ratio is in the range $100\text{--}1000$, the activity is extremely high and complete conversions can be reached in a few minutes, nevertheless a quite good activity is also obtained at very low Al/Co molar ratio ($20\text{--}50$).
- (v) The polymerization rate is higher and more stereoregular polymers (higher 1,2 content and higher syndiotacticity) are obtained when heptane instead of toluene is used as polymerization solvent, indicating that the aromatic solvent can in some way coordinate to the metal atom affecting the catalyst geometry and competing with the incoming monomer. This phenomenon is not however surprising because a similar solvent effect was already observed for instance in the polymerization of 1,3-dienes with neodymium catalysts [7].

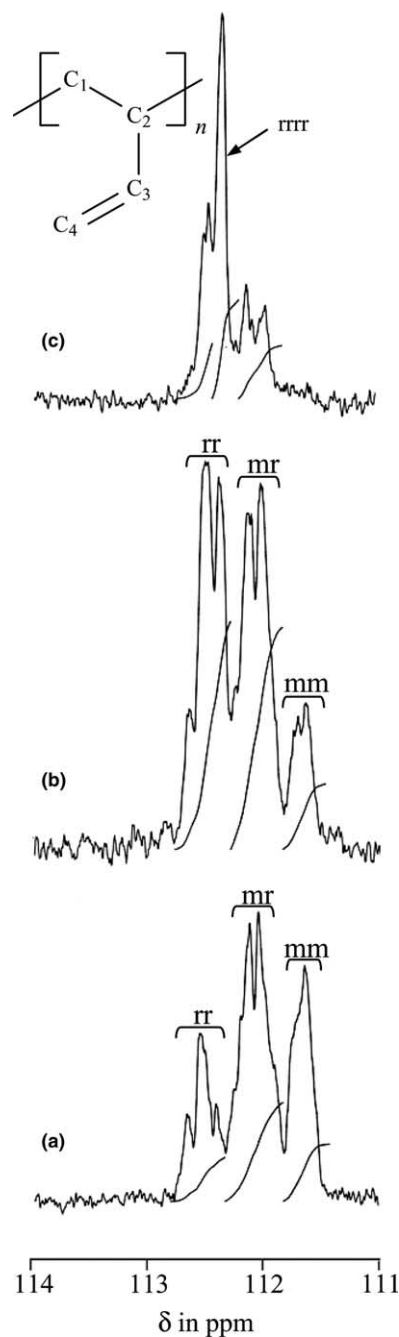


Fig. 5. ^{13}C NMR spectrum (olefinic region, C4 signal; $\text{C}_2\text{D}_2\text{Cl}_4$, HMDS as internal standard, 103°C) of the polybutadienes obtained with (a) $\text{CoCl}_2(\text{PMePh}_2)_2\text{-MAO}$ (Table 5, run 3); (b) $\text{CoCl}_2(\text{P}^n\text{PrPh}_2)_2\text{-MAO}$ (Table 5, run 7); (c) $\text{CoCl}_2(\text{PCyPh}_2)_2\text{-MAO}$ (Table 5, run 13).

- (vi) We have also examined the polymerization of butadiene with the systems $\text{CoCl}_2(\text{PR}_2\text{Ph})_2\text{-MAO}$ (Table 5, runs 16–19); essentially 1,2 polymers were obtained also in this case but the syndiotactic index of the polymers, at the same polymerization conditions, was in general slightly lower with respect to that of the 1,2 polybutadienes obtained with $\text{CoCl}_2(\text{PRPh}_2)_2\text{-MAO}$.

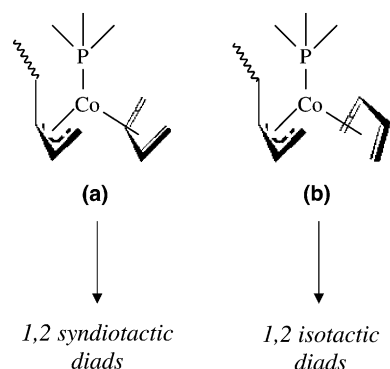


Fig. 6. Possible reciprocal orientation ((a) *exo-exo*; (b) *exo-endo*) of the butadiene of the allylic unit of the polymer growing chain and of the butadiene entering monomer.

The formation of 1,2 polymers having different tacticity depending on the type of phosphine ligand, in the polymerization of butadiene with the cobalt systems of this paper, is not an absolute novelty. A similar behavior has already been observed in the polymerization of butadiene with $\text{CrCl}_2(\text{L})_2$ -MAO systems (L = bidentate phosphine ligand) [8]. The interpretation given at that time for such a behavior, based on the diene polymerization mechanism proposed by Porri et al. [9], is still valid and can also be applied to the cobalt catalysts described in this paper. The incoming butadiene monomer and the allylic unit of the growing polymer chain can assume the two different orientations shown in Fig. 6. 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; when the steric demand of the ligand is higher (e.g., P^iPrPh_2 , PCyPh_2 , and PCy_2Ph), the *exo-exo* orientation is the favored one and predominantly syndiotactic polymers are obtained.

3. Conclusion

New cobalt phosphine complexes have been synthesized by reacting cobalt (II) chloride with various diphenylalkylphosphines. In the case of $\text{CoCl}_2(\text{PEtPh}_2)_2$, $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ and $\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$, single crystals have been obtained allowing us to determine their molecular structure.

All these complexes were then used in association with MAO for the polymerization of 1,3 butadiene; they were found to be highly active catalysts giving polymers having an essentially 1,2 structure. This result is quite interesting, since it is known that 1,2 polybutadiene plays an important role in the field of butadiene polymers, being the only polymer together with *cis*-1,4 polybutadiene industrially produced.

Moreover by varying the alkyl group bonded to the phosphorous atom, i.e., the ligand hindrance, it was pos-

sible to obtain 1,2 polybutadienes having different melting point, crystallinity degree and tacticity, the syndiotacticity increasing with increasing the steric hindrance of the alkyl group.

Finally, the results obtained have also some mechanistic implications; they can be interpreted on the basis of the diene polymerization mechanism proposed by Porri, confirming, if still necessary, its validity and supporting some aspects of the same mechanism, in particular the influence of the ligand on the stereoselectivity.

4. Experimental

4.1. General procedures and materials

Methyldiphenylphosphine (Strem, 99% pure), dimethyldiphenylphosphine (Strem, 99% pure), *normal*-propyldiphenylphosphine (Aldrich, 98% pure), ethyldiphenylphosphine (Aldrich, 98% pure), diethyldiphenylphosphine (Aldrich, 96% pure), allyldiphenylphosphine (Aldrich, 95% pure), diallyldiphenylphosphine (Aldrich, 95% pure), *iso*-propyldiphenylphosphine (Aldrich, 97% pure), cyclohexyldiphenylphosphine (Strem, 98% pure), dicyclohexyldiphenylphosphine (Aldrich, 95% pure), anhydrous cobalt dichloride (Aldrich, 99.9% pure), and methylaluminoxane (MAO) (Crompton, 10 wt% solution in toluene) were used as received. Ethyl alcohol (Carlo Erba, 96%) was degassed under vacuum, then by bubbling dry dinitrogen and kept over molecular sieves; pentane (Carlo Erba, >99% pure) was refluxed over Na/K alloy for ca. 8 h, then distilled and stored over molecular sieves under dry dinitrogen; toluene (Carlo Erba, 99.5% pure) was refluxed over Na for ca. 8 h, then distilled and stored over molecular sieves under dry dinitrogen. 1,3-Butadiene (Air Liquide, >99.5% pure) was evaporated from the container before each run, dried by passing through a column packed with molecular sieves and condensed into the reactor which had been precooled to -20°C . All the phosphine cobalt complexes were synthesized as indicated below, following a general procedure already reported in the literature [6]. Infrared spectra of the cobalt complexes were recorded as KBr disks with a Bruker IFS 48 instrument.

4.2. Synthesis of cobalt phosphine complexes

4.2.1. $\text{CoCl}_2(\text{PMePh}_2)_2$

Methyldiphenylphosphine (4.00 g, 1.82×10^{-2} mol) was added to a solution of CoCl_2 (1.06 g, 8.20×10^{-3} mol) in ethanol (100 ml). A blue precipitate is immediately formed; after 20 h it was filtered, washed with ethyl alcohol (2×10 ml) and pentane (2×10 ml), then dried in vacuum at room temperature. The blue solid isolated was transferred on the filter of a Soxhlet for solids and extracted in continuous with boiling toluene.

The extraction was practically complete in two days; at the end a crystalline blue product is formed on the bottom of the extraction Schlenck-tube. The blue supernatant solution was removed, concentrated and cooled at $-30\text{ }^{\circ}\text{C}$, causing the precipitation of a crystalline product. Further crops of crystals were obtained by repeating this work-up operation several times. Yield: 3.49 g (80% based on CoCl_2).

Anal. Calc. for $\text{C}_{26}\text{H}_{26}\text{CoCl}_2\text{P}_2$: Co, 11.11; Cl, 13.37; P, 11.68. Found: Co, 10.9; Cl, 13.2; P, 11.3%.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3053m, 3009w, 2988w, 1484m, 1437s, 1416m, 1332w, 1314w, 1289w, 1186w, 1100m, 1073w, 1026w, 999w, 888s, 844w, 757m, 739s, 694s, 507s, 472m, 436w, 419w.

4.2.2. $\text{CoCl}_2(\text{PMe}_2\text{Ph})_2$

Dimethylphenylphosphine (2.2 g; 1.65×10^{-3} mol) was added to a solution of CoCl_2 (1.07 g, 8.2×10^{-3} mol) in ethanol (60 ml). A dark-blue solution is immediately formed; it was kept under stirring at room temperature for 24 h, then the solvent was removed under vacuum. The residue was washed with ethanol (2×10 ml) at low temperature and with pentane (3×20 ml) and then dried under vacuum at room temperature. Yield: 2.6 g (80% based on CoCl_2).

Anal. Calc. for $\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{CoP}_2$: Co, 14.51; Cl, 17.46; P, 15.25. Found: Co, 14.2; Cl, 17.7; P, 15.4%.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3076w, 2971m, 2907m, 1489m, 1435s, 1420s, 1322w, 1305m, 1288w, 1136m, 1107ms, 1029w, 1001w, 953s, 906s, 873m, 837w, 747s, 717m, 690s, 677m, 484s.

4.2.3. $\text{CoCl}_2(\text{PEtPh}_2)_2$

Ethylidiphenylphosphine (2.1 g; 9.75×10^{-3} mol) was added to a solution of CoCl_2 (0.55 g, 4.24×10^{-3} mol) in 60 ml of ethyl alcohol. A blue precipitate is immediately formed; it was kept under stirring for 20 h then it was filtered. The residue was washed with ethyl alcohol (2×10 ml), then dried under vacuum. The blue solid isolated was then transferred on the filter of a Soxhlet for solids and extracted in continuous with boiling toluene. The solubility in toluene is very high and the extraction was practically completed in a few hours. At the end a crystalline blue product is present on the bottom of the extraction Schlenck, and further crops of crystals can be isolated by concentration and cooling of the supernatant. Yield: 2.2 g (94% based on CoCl_2).

Anal. Calc. for $\text{C}_{28}\text{H}_{30}\text{CoCl}_2\text{P}_2$: Co, 10.56; Cl, 12.70; P, 11.10. Found: Co, 10.6; Cl, 13.0; P, 11.2%.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3050m, 2978m, 2965m, 2932m, 2907m, 2877m, 1484ms, 1457ms, 1435s, 1411m, 1385m, 1336w, 1313w, 1275w, 1251w, 1185m, 1161w, 1126w, 1102s, 1072w, 1028w, 1000s, 854w, 769ms, 742s, 695s, 674m, 512s, 480s, 461m, 418w.

4.2.4. $\text{CoCl}_2(\text{PEt}_2\text{Ph})_2$

Diethylphenylphosphine (2.1 g, 9.75×10^{-3} mol) was added to a solution of CoCl_2 (0.26 g, 2×10^{-3} mol) in ethyl alcohol (60 ml). The dark blue solution formed was stirred at room temperature for 24 h, then the solvent was removed under vacuum. The residue obtained was washed with pentane (3×20 ml), dried under vacuum and then extracted in continuous with boiling toluene for ca. 24 h. The blue solution obtained was concentrated, and a large excess of pentane was added causing the formation of a blue precipitate which was filtered off and dried under vacuum. Yield, 0.66 g (69% based on CoCl_2).

Anal. Calc. for $\text{C}_{20}\text{H}_{30}\text{Cl}_2\text{CoP}_2$: Co, 12.75; Cl, 15.34; P, 13.4. Found: Co, 12.4; Cl, 15.5; P, 13.0%.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 2961m, 2934m, 2873m, 2855m, 1462s, 1435ms, 1378m, 1102ms, 1072w, 1043m, 1032m, 856w, 777m, 748m, 732m, 722m, 713m, 694m, 639m, 513s.

4.2.5. $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$

Propyldiphenylphosphine (4 g, 1.75×10^{-2} mol) was introduced on an ethanol solution (60 ml) of CoCl_2 (1.06 g, 8.16×10^{-3} mol). The reaction was stirred for about 24 h, then the blue precipitate formed was separated by filtration, washed with ethyl alcohol and dried under vacuum. The blue solid was then transferred on the filter of a Soxhlet for solids and extracted in continuous with boiling pentane. The solubility is not very high, so the extraction was continued for several days. A crystalline product is formed during the extraction, which was separated by removing the supernatant and dried under vacuum. Yield: 4.09 g (85% based on CoCl_2).

Anal. Calc. for $\text{C}_{30}\text{H}_{34}\text{CoCl}_2\text{P}_2$: Co, 10.05; Cl, 12.09; P, 10.56. Found: Co, 10.0; Cl, 12.4; P, 10.2%.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3051w, 2964m, 2938m, 2894w, 2873w, 1484m, 1450w, 1434s, 1408w, 1376w, 1332w, 1313w, 1187w, 1101s, 1080m, 1029m, 853w, 837m, 755s, 730ms, 696s, 513s, 482ms, 459w, 417w.

4.2.6. $\text{CoCl}_2[\text{P}(\text{allyl})\text{Ph}_2]_2$

A solution of CoCl_2 (0.191 g, 1.4×10^{-3} mol) in ethyl alcohol (10 ml) was added to an ethanol solution (40 ml) of allyldiphenylphosphine (1 g, 4.42×10^{-3} mol). The solution became dark blue; it was stirred for ca. 24 h, then the solvent was removed under vacuum. The blue residue was washed with small amounts of ethanol at low temperature and with pentane (2×10 ml) and finally dried in vacuum. Yield: 0.582 g (68% based on CoCl_2).

Anal. Calc. for $\text{C}_{24}\text{H}_{30}\text{CoCl}_2\text{P}_2$: Co, 10.12; Cl, 12.18; P, 10.64. Found: Co, 9.9; Cl, 12.3; P, 10.3%.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 1635m, 1484w, 1464m, 1435s, 1377m, 1099m, 988m, 923m, 839m, 740s, 691s.

4.2.7. $\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$

Bis-allylphenylphosphine (2 g, 1.05×10^{-2} mol) was added to an ethanol solution (35 ml) of CoCl_2 (0.55 g, 4.21×10^{-3} mol). The dark blue solution immediately formed was stirred for one night at room temperature, then the solvent was removed under vacuum. The residue was washed several times with pentane; at the end a blue solid is isolated. It was dissolved in toluene and a crystalline product was obtained by cooling the solution at -30°C . Further crops of crystals were obtained by concentration and cooling of the supernatant. Yield: 1.32 g (69% based on CoCl_2).

Anal. Calc. for $\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{CoP}_2$: Co, 11.55; Cl, 13.90; P, 12.14. Found: Co, 11.4; Cl, 13.8; P, 11.9%.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3083w, 3057w, 3013w, 2978w, 2942w, 2899w, 1637ms, 1592w, 1487w, 1437s, 1421m, 1397m, 1262w, 1205m, 1152s, 1114s, 1074m, 996m, 932s, 852m, 833m, 748s, 694s, 631ms, 593m, 491m.

4.2.8. $\text{CoCl}_2(\text{PCyPh}_2)_2$

Cyclohexyldiphenylphosphine (4.85 g, 1.81×10^{-2} mol) dissolved in ethanol (60 ml) was added to an ethanol solution (60 ml) of CoCl_2 (1.065 g, 8.2×10^{-3} mol). A blue precipitate is rapidly formed; the suspension was stirred for ca. 20 h, then filtered. The blue residue on the filter was washed with ethanol (2×10 ml) and pentane (2×10 ml), then dried under vacuum. The blue solid was then transferred on the filter of a Soxhlet for solids and extracted in continuous with boiling pentane. The solubility is moderate and the extraction was continued for several days. A crystalline product increasing with time is formed during the extraction. At the end the pentane solution is removed and the crystals are dried under vacuum. Yield: 4.74 g (87% based on CoCl_2).

Anal. Calc. for $\text{C}_{36}\text{H}_{42}\text{CoCl}_2\text{P}_2$: Co, 8.84; Cl, 10.64; P, 9.29. Found: Co, 9.0; Cl, 10.5; P, 9.4%.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3056w, 2934s, 2853m, 1626s, 1482m, 1453s, 1372w, 1336w, 1264w, 1185mw, 1100ms, 1027mw, 999mw, 889w, 802mw, 745s, 694s, 618w, 527s, 516s, 499ms, 460mw.

4.2.9. $\text{CoCl}_2(\text{PCy}_2\text{Ph})_2$

Dicyclohexylphenylphosphine (1 g, 3.64×10^{-3} mol) dissolved in ethanol (50 ml) was added to an ethanol solution (20 ml) of CoCl_2 (0.19 g, 1.46×10^{-3} mol). After a few minutes, a blue-turquoise suspension is formed. It was kept under stirring for one night, then the solvent was partially removed and the blue precipitate filtered off. The residue on the filter was washed with ethanol (3×10 ml) and pentane (3×10 ml), then dried under vacuum. The residue was successively extracted in continuous with boiling toluene for a few days; the blue extraction solution was concentrated and a large excess of pentane was added causing the precipitation of a blue powder. Yield, 0.85 g (86% conversion based on CoCl_2).

Anal. Calc. for $\text{C}_{36}\text{H}_{54}\text{Cl}_2\text{CoP}_2$: Co, 8.68; Cl, 10.45; P, 9.13. Found: Co, 8.4; Cl, 10.6; P, 9.0%.

Spectroscopic data: IR (KBr) ν (cm^{-1}), 2954w, 2919s, 2853mw, 1626s, 1462s, 1377m, 1342w, 1268w, 1182mw, 999mw, 887w, 749s, 727m, 698s, 523s.

4.3. X-ray crystallographic studies

A summary of the experimental details concerning the X-ray diffraction study of $\text{CoCl}_2(\text{PEtPh}_2)_2$, $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ and $\text{CoCl}_2[\text{P}(\text{allyl})_2\text{Ph}]_2$ is reported in Table 4. The crystals used for data collection were entirely covered with perfluorinated oil to reduce crystal decay. X-ray data were collected on a Bruker Smart Apex CCD area detector equipped with fine-focus sealed tube operating at 50 kV and 30 mA. The first 100 frames were collected also at the end of the data collection to monitor crystal decay. Data reduction was made using SAINT programs; absorption corrections based on multi-scan were obtained by SADABS [10]. The structures were solved by SIR 92 [11] and refined on F^2 by full-matrix least-squares using SHELX 97 [12]. The program ORTEP-III [13] was used for molecular graphics.

4.4. Polymerization

All operations were carried out under an atmosphere of dry dinitrogen. A standard procedure is reported. 1,3-Butadiene was condensed into a 25 mL dried glass reactor kept at -20°C , then toluene was added and the solution so obtained was brought to the desired polymerization temperature. Methylaluminoxane (MAO) and the cobalt compound were then added, as toluene solutions, in the order. The polymerization was terminated with methanol containing a small amount of hydrochloric acid, the polymer was coagulated and repeatedly washed with methanol, then dried in vacuum at room temperature.

4.5. Polymer characterization

^{13}C NMR and ^1H NMR measurements were performed with a Bruker AM 270 instrument. The spectra were obtained in $\text{C}_2\text{D}_2\text{Cl}_4$ at 103°C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was about 10 wt%. Differential scanning calorimetry (DSC) scans were carried out on a Perkin Elmer Pyris 1 instrument. Typically, ca. 10 mg of polymer were analyzed in each run, while scan speed was ca. 20 K/min under a dinitrogen atmosphere. X-ray diffraction powder spectra of the polymers were recorded on an Italstructure θ/θ diffractometer. The infrared spectra were performed with a Bruker IFS 48 instrument, using polymer films on KBr disks. The films were obtained by deposition from solutions in benzene or hot (ca. 100°C) solutions in 1,2,4-trichlorobenzene.

The molecular weight averages (MW) and the molecular weight distribution (MWD) were obtained by a high temperature GPCV 2000 system (from Waters) using two on-line detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three Olefi columns from PSS, *o*-dichlorobenzene as mobile phase, 0.8 mL/min of flow rate and 145 °C of temperature. The calibration of the GPC system was constructed by eighteen narrow MWD polystyrene standards with the molar mass ranging from 162 to 3.3×10^6 g/mol.

5. Supplementary material

Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles of $\text{CoCl}_2(\text{PEtPh}_2)_2$, $\text{CoCl}_2(\text{P}^i\text{PrPh}_2)_2$ and $\text{CoCl}_2(\text{P}(\text{allyl})_2\text{Ph})_2$ may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on quoting the deposition numbers CCDC 258333, 258334 and 258335, respectively, the names of the authors and the journal citation (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; web site: <http://www.ccdc.cam.ac.uk>).

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References

- [1] G. Ricci, A. Forni, A. Boglia, T. Motta, *J. Mol. Cat. A: Chem.* 226 (2005) 235.
- [2] G. Ricci, A. Forni, A. Boglia, T. Motta, G. Zannoni, M. Canetti, F. Bertini, *Macromolecules* 38 (2005) 1064.
- [3] G. Ricci, A. Boglia, A. Forni, R. Santi, A. Sommazzi, F. Masi, Italian Patent MI03A 001808, 23/09/2003.
- [4] C.A. Tolman, *Chem. Rev.* 77 (1977) 313.
- [5] (a) G. Ricci, A. Boglia, R. Santi, A. Sommazzi, F. Masi, Italian Patent MI03A 001807, 23/09/2003; (b) G. Ricci, A. Boglia, R. Santi, A. Sommazzi, F. Masi, Italian Patent MI03A 001809, 23/09/2003.
- [6] J. Chatt, B.L. Shaw, *J. Chem. Soc.* (1961) 285.
- [7] G. Ricci, G. Boffa, L. Porri, *Makromol. Chem., Rapid Commun.* 7 (1986) 355.
- [8] (a) G. Ricci, M. Battistella, L. Porri, *Macromolecules* 34 (2001) 5766; (b) G. Ricci, A. Forni, A. Boglia, M. Sonzogni, *Organometallics* 23 (2004) 3727.
- [9] (a) L. Porri, in: F. Ciardelli, P. Giusti (Eds.), *Structural Order in Polymers*, Pergamon Press Ltd., Oxford, 1981, p. 51; (b) L. Porri, A. Giarrusso, G. Ricci, *Prog. Polym. Sci.* 16 (1991) 405; (c) L. Porri, A. Giarrusso, G. Ricci, *Makromol. Chem., Macromol. Symp.* 48/48 (1991) 239; (d) L. Porri, A. Giarrusso, G. Ricci, *Macromol. Symp.* 178 (2002) 55.
- [10] Bruker, SMART, SAINT and SADABS; Bruker AXS Inc.: Madison Wisconsin, USA, 1997.
- [11] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* 27 (1994) 435.
- [12] G.M. Sheldrick, *SHELX-97*. Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen Germany, 1997.
- [13] M.N. Burnett, C.K. Johnson, *ORTEP-III: Oak ridge thermal ellipsoid plot program for crystal structure illustrations*, Oak Ridge National Laboratory Report ORNL-6895, 1996.