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Articles

Synthesis and X-ray Structure of $CoCl_2(P^iPrPh_2)_2$. A New Highly Active and Stereospecific Catalyst for 1,2 Polymerization of Conjugated Dienes When Used in Association with MAO

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ABSTRACT: The new cobalt (II) phosphine complex $CoCl_2(P^iPrPh_2)_2$ was synthesized by reacting $CoCl_2$ with isopropyldiphenylphosphine in ethyl alcohol as solvent. The molecular structure of the complex was determined by the X-ray diffraction method. $CoCl_2(P^iPrPh_2)_2$ was then used in combination with methylaluminoxane for the polymerization of 1,3-butadiene: it was found to be highly active and stereospecific for the preparation of 1,2 syndiotactic polybutadiene. The same system was also able to polymerize substituted butadienes giving highly stereoregular 1,2 polymers from *E*-1,3-pentadiene, 1,3-hexadiene, and 3-methyl-1,3-pentadiene. Some of these polymers are completely new and were never prepared before.

Introduction

We have recently reported on the synthesis of alkylphosphine cobalt complexes and their use in combination with methylaluminoxane (MAO) in the polymerization of 1,3-butadiene.[1] These systems gave polymers having different structure (predominantly 1,2; mixed *cis*-1,4/1,2 structure; *cis*-1,4) depending on the type of phosphine ligand bonded to the metal. We wanted to examine also the polymerization of butadiene with catalysts based on cobalt complexes with aromatic phosphines ($CoCl_2(PRPh_2)_2$; $CoCl_2(PR_2Ph)_2$; R = alkyl, cycloalkyl, or allyl group); it has been reported in the literature that the catalyst $CoBr_2(PPh_3)_2$−MAO gives from butadiene a polymer with a mixed *cis*-1,4/1,2 structure exhibiting a very high activity.[2] In the course of this investigation, we synthesized the new cobalt complex $CoCl_2(P^iPrPh_2)_2$ by reacting $CoCl_2$ with isopropyldiphenylphosphine in ethyl alcohol as solvent. The molecular structure of this complex was determined by the X-ray diffraction method, then it was used in association with MAO for the polymerization of butadiene and other substituted butadienes (isoprene, 1,3-pentadiene, 1,3-hexadiene, 3-methyl-1,3-pentadiene). The resulting catalyst system was found to be highly active and stereospecific, giving essentially 1,2 polymers from the different monomers cited above; some of these diene polymers are completely new and were never prepared before. The most significant results obtained are reported in the present paper.

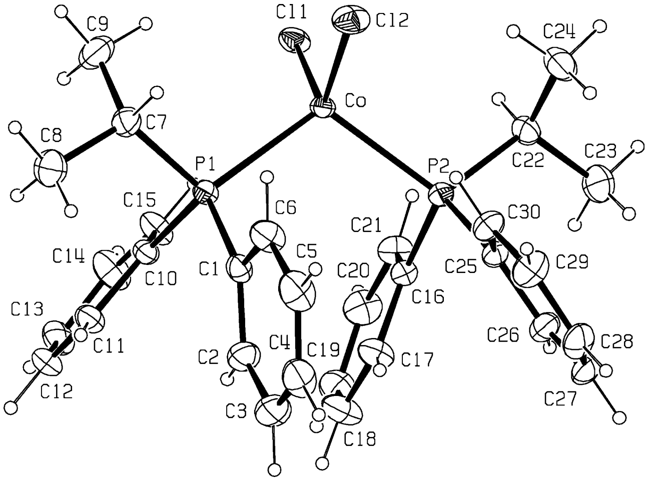

Figure 1. ORTEP plot[30] of $CoCl_2(P^iPrPh_2)_2$ with atom numbering scheme. Displacement ellipsoids are drawn at the 20% probability.

Results and Discussion

Synthesis and Characterization of $CoCl_2(P^iPrPh_2)_2$. $CoCl_2(P^iPrPh_2)_2$ was synthesized following a general experimental procedure previously reported for these types of compounds.[3] Single crystals suitable for X-ray structure determination were obtained by crystallization from pentane solution at low temperature (−30 °C). The molecular structure is shown in Figure 1, and selected bond lengths and angles are reported in Table 1. The Co(II) environment in $CoCl_2(P^iPrPh_2)_2$ is approximately tetrahedral, where the largest deviations from the ideal tetrahedral coordination are ascribed to the mutual repulsion between the chlorine atoms. A close similarity is found between the title complex and

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for $CoCl_2(P^{i}PrPh_2)_2$

	Bond Lengths		
Co−Cl1	2.2276(7)	P1−C7	1.847(2)
Co−Cl2	2.2023(8)	P1−C10	1.816(2)
Co−P1	2.3708(7)	P2−C16	1.813(2)
Co−P2	2.3549(7)	P2−C22	1.853(2)
P1−C1	1.825(2)	P2−C25	1.810(2)
	Bond Angles		
Cl1−Co−Cl2	114.25(3)	C1−P1−C10	107.64(11)
P1−Co−P2	110.64(3)	C1−P1−C7	104.82(12)
Cl1−Co−P1	112.58(3)	C10−P1−C7	106.12(11)
Cl1−Co−P2	102.10(3)	C16−P2−C25	106.37(11)
Cl2−Co−P1	104.79(3)	C16−P2−C22	106.45(12)
Cl2−Co−P2	112.69(3)	C25−P2−C22	105.59(11)

the other two previously reported structures of tetracoordinated Co(II) dichloro−diphosphine complexes, that is, $CoCl_2(PPh_3)_2$ [4] and $CoCl_2(PPh_2CHC(O)Ph)_2$.[5] A comparison between corresponding bond lengths in these three related complexes indicates that the average Co−Cl distances, 2.215(1) Å in $CoCl_2(P^{i}PrPh_2)_2$, are the same within 0.01 Å, while significant though small differences are observed in the Co−P distances. The shortest values are found in the title complex, 2.363(1) Å on average, to be compared with 2.384(1) and 2.399(2) Å for the corresponding distances in $CoCl_2(PPh_3)_2$ [4] and in $CoCl_2(PPh_2CHC(O)Ph)_2$,[5] respectively. This denotes a slightly greater basicity for the phosphine ligand of the former complex.

From a sterical point of view, the two $P^{i}PrPh_2$ and PPh_3 phosphine ligands appear to be very similar, as denoted by both the bond angles on the P atom, which fall in the range 104.8(1)−107.6(1)° in both structures, and the Tolman cone angles.[6] Using the actual Co−P bond distances as determined from the X-ray measurements, instead of the fixed value of 2.28 Å,[6] and a van der Waals radius of 1.2 Å for the hydrogen atom, effective cone angles of 155° and 150° were calculated for the two phosphine ligands of $CoCl_2(P^{i}PrPh_2)_2$ containing atoms P1 and P2, respectively. These values are in excellent agreement with the cone angle reported by Tolman for $P^{i}PrPh_2$, 150°, which is in turn very close to the tabulated value for PPh_3, 145°.[6]

Polymerization of 1,3-Butadiene. The results obtained by polymerizing butadiene with the system $CoCl_2(P^{i}PrPh_2)_2$-MAO are reported in Table 2 and can be summarized as follows.

The system $CoCl_2(P^{i}PrPh_2)_2$−MAO gives from butadiene crystalline polymers (Figure 2a) having an essentially 1,2 structure; such a structure was attributed on the basis of the FT-IR, ^{13}C, and ^{1}H NMR spectra (Figures 3a, 4, and 5, respectively), according to what is already reported in the literature.[7] The polymer 1,2 content, determined from the ^{1}H NMR[7b,d] spectra as reported in the Experimental Section, depends on the polymerization conditions: it slightly increases with a decrease in the MAO/Co molar ratio (cf. runs 1−5 and 7−8 in Table 2) and the polymerization temperature (cf. runs 6−7 in Table 2).

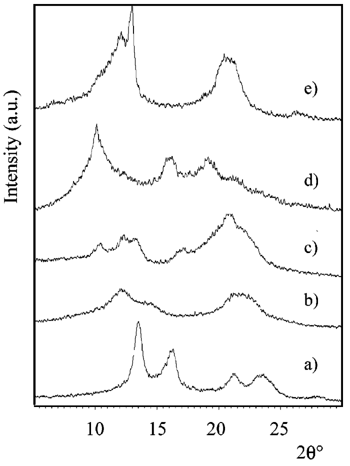

Figure 2. X-ray powder spectra of (a) polybutadiene (Table 2, run 8); (b) polypentadiene (Table 3, run 2); (c) polyhexadiene (Table 3, run 3); and (d) poly(3-methyl-1,3-pentadiene) (Table 3, run 4) obtained with the system $CoCl_2(P^{i}PrPh_2)_2$−MAO and (e) poly(3-methyl-1,3-pentadiene) obtained with $FeCl_2(bipy)_2$−MAO (Table 3, run 5).

All the polybutadienes obtained have an essentially syndiotactic structure; in fact, in the ^{13}C NMR spectrum (Figure 4), the peak at 112.31 ppm, corresponding to the syndiotactic pentad rrrr,[7e,g] is predominant, while in the ^{1}H NMR spectrum (Figure 5), the signal centered at 1.13 ppm, corresponding to the aliphatic methylene protons, is a false triplet, which is typical of a 1,2 syndiotactic structure.[8] The syndiotactic index (percentage of syndiotactic pentads, [rrrr]) determined from the ^{13}C NMR spectra[7e,g] is in the range 45−65%, increasing with a decrease in the polymerization temperature. The melting points of the different polybutadienes (Figure 6a) are in the range 120−164 °C and in general increase with an increase in the polymer syndiotacticity.

Polymers obtained using heptane as polymerization solvent are, at the same polymerization conditions, more stereoregular (higher 1,2 content and higher syndiotactic content) than those obtained in aromatic solvent (cf. runs 1 and 6 in Table 2). This seems to indicate that toluene can in some way coordinate to the metal affecting both chemo- and stereoselectivity.

Table 2. Polymerization of Butadiene with the System $CoCl_2(P^{i}PrPh_2)_2$−MAO[a]

	polymerization					polymer					
run	solvent	Al/Co (molar ratio)	temp (°C)	time (min)	conv (%)	*cis*-1,4[b] (%)	1,2[b] (%)	[rrrr][c]	mp[d] (°C)	MW[e] (g mol−1)	MWD[e]
1	toluene	1000	+20	7	58.5	24.1	75.9	46.4	120	−	−
2	toluene	500	+20	5	48.9	20.5	79.5	45.8	121	−	−
3	toluene	100	+20	2	30.0	14.6	85.4	47.6	126	−	−
4	toluene	50	+20	30	50.5	14.3	85.7	47.0	124	−	−
5	toluene	20	+20	40	40.7	14.0	86.0	48.1	130	−	−
6	heptane	1000	+20	2	100	14.2	85.8	47.7	128	187000	2.6
7	heptane	1000	−30	140	35.7	12.1	87.9	60.4	159	226000	2.3
8	heptane	100	−30	270	100	10.9	89.1	63.2	164	211000	2.4

[a] Polymerization conditions: butadiene, 2 mL; solvent total volume, 16 mL; MAO; $CoCl_2(P^{i}PrPh_2)_2$, 3×10^{-6} moles. [b] Determined by NMR analysis (^{13}C and ^{1}H NMR). [c] Percentage of syndiotactic pentads, determined by ^{13}C NMR. [d] Determined by DSC. [e] Molecular weight and molecular weight distribution determined by GPC analyses; polymers obtained in toluene as solvent were rather insoluble.

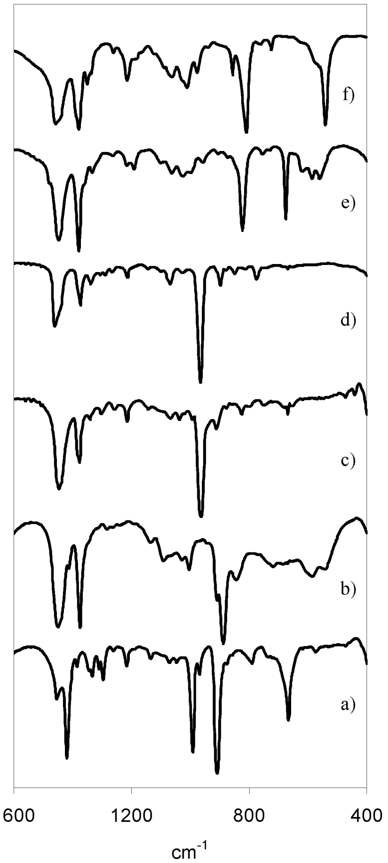

Figure 3. FT-IR spectra of (a) polybutadiene (Table 2, run 8); (b) polyisoprene (Table 3, run 1); (c) polypentadiene (Table 3, run 2); (d) polyhexadiene (Table 3, run 3); and (e) poly(3-methyl-1,3-pentadiene) (Table 3, run 4) obtained with the system $CoCl_2(P^iPrPh_2)_2$−MAO and (f) poly(3-methyl-1,3-pentadiene) obtained with the system $FeCl_2(bipy)_2$−MAO (Table 3, run 5).

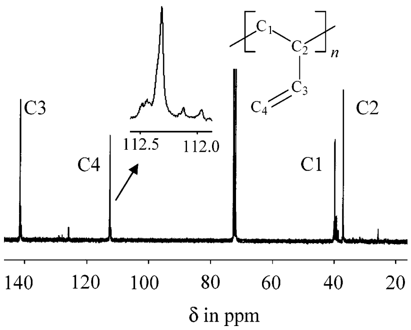

Figure 4. ^{13}C NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of the polybutadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO at −30 °C (Table 2, run 8).

The catalyst activity is extremely high when MAO/Co molar ratio is in the range 100−1000, nevertheless a good activity is also observed at lower MAO/Co ratios (≤ 50), meaning that the alkylation of the cobalt compound is rather fast and that a certain number of active sites are formed also in these polymerization conditions.

Polymerization of Substituted Butadienes. The system $CoCl_2(P^iPrPh_2)_2$−MAO, unlike other cobalt systems giving highly syndiotactic polybutadiene (e.g., $(C_4H_6)Co(\eta^5\text{-}C_8H_{13})/CS_2$; $Co(acac)_3$−$AlEt_3$−CS_2),[9] was also found to be able to polymerize substituted butadienes such as isoprene, *E*-1,3-pentadiene, 1,3-hexadiene, and 3-methyl-1,3-pentadiene. The results obtained in these polymerizations are shown in Table 3 and can be summarized as follows.

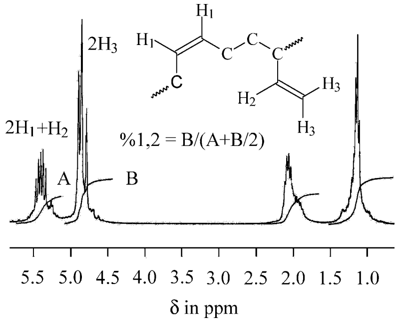

Figure 5. ^1H NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of the polybutadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO at −30 °C (Table 2, run 8).

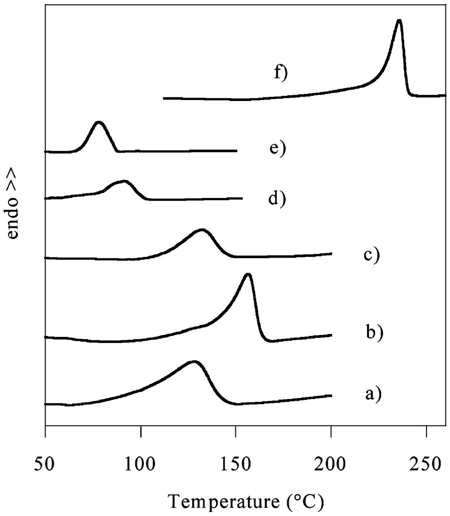

Figure 6. DSC thermograms of (a) polybutadiene (Table 2, run 3); (b) polybutadiene (Table 2, run 8); (c) polypentadiene (Table 3, run 2); (d) polyhexadiene (Table 3, run 3); and (e) poly(3-methyl-1,3-pentadiene) (Table 3, run 4) obtained with $CoCl_2(P^iPrPh_2)_2$−MAO and (f) poly(3-methyl-1,3-pentadiene) obtained with the system $FeCl_2(bipy)_2$−MAO (Table 3, run 5).

The system $CoCl_2(P^iPrPh_2)_2$−MAO gives from isoprene (Table 3, run 1) a polymer having a mixed *cis*-1,4/3,4 structure; a small amount of 1,2 units are also present. This structure is deduced from the polymer FT-IR spectrum (Figure 3b) in which two intense bands at 890 and 840 cm^{-1} due to 3,4 and 1,4 units, respectively, and a less intense band at 911 cm^{-1} due to 1,2 units can be detected.[10] The presence of a band at 1375 cm^{-1} is indicative of a cis configuration of the double bond, being the same band at 1385 cm^{-1} in the case of a trans double bond.[10] The polymer is not crystalline, and no melting point was detected. The ^{13}C spectrum is shown in Figure 7; the different peaks were assigned on the basis of what is already reported in the literature[11] and are consistent with the polymer microstructure indicated above. Further work is in progress in order to determine the type of distribution of the different units along the polymer chain; nevertheless, the fact that the resonances assigned to the cis units correspond to those observed in the *cis*-1,4 polyisoprene is indicative of the presence of cis sequences.

$CoCl_2(P^iPrPh_2)_2$−MAO gives from *E*-1,3-pentadiene a crystalline polymer, as indicated by its X-ray powder spectrum (Figure 2b), with a melting point of 132 °C (Figure 6c). The IR spectrum of the polymer is shown in Figure 3c; the absence of any band at 750 and 911

Table 3. Polymerization of Substituted Butadienes with $CoCl_2(P^iPrPh_2)_2$−MAO[a]

				polymer microstructure[b]				
run	monomer	time (h)	conv (%)	*cis*-1,4 (%)	1,2 (%)	mp[c] (°C)	MW[d] (g mol^{-1})	MWD[d]
1	I	5	100	43	57[d]	–	37000	1.9
2	EP	2	67		~99	132	180000	2.3
3	H	4	45		~99	89	177000	2.2
4	3MP	72	70		~99	79	45000	1.6
5[e]	3MP	240	68		~99[f]	242	–	

[a] Polymerization conditions: momoner, 2 mL; toluene, total volume 16 mL; MAO/Co = 100; $CoCl_2(P^iPrPh_2)_2$, 2×10^{-5} mol; +20 °C. I = isoprene; EP = *E*-1,3-pentadiene; H = 1,3-hexadiene; 3MP = 3-methyl-1,3-pentadiene. [b] Determined by IR and NMR (^{13}C and ^1H NMR) analysis. [c] Determined by DSC analysis. [d] 3,4 units. [e] $FeCl_2(bipy)_2$ was used instead of $CoCl_2(P^iPrPh_2)_2$, and the polymerization was carried out at −30 °C. [f] Determined by IR (KBr) analysis since the polymer is practically insoluble.

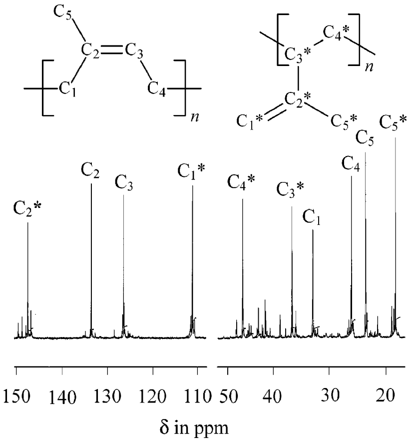

Figure 7. ^{13}C NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of the polyisoprene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 3, run 1).

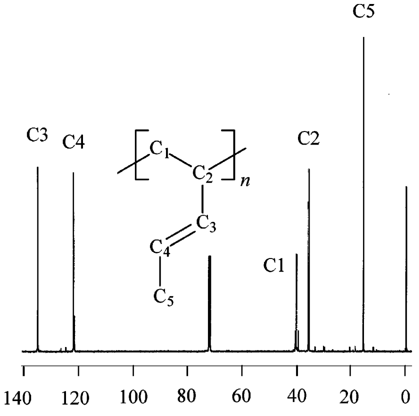

Figure 8. ^{13}C NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of the polypentadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 3, run 2).

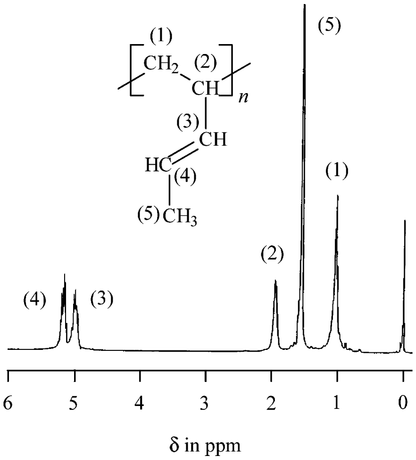

Figure 9. ^1H NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of the polypentadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 3, run 2).

cm^{-1} excludes the presence of *cis*-1,4 and 3,4 units, respectively, while the presence of an intense band at 963 cm^{-1} clearly indicates that the polymer has a *trans*-1,2 structure, being the same band in a *trans*-1,4 structure at 966 cm^{-1}.[12] The 1,2 structure is confirmed by the presence of the band at 1376 cm^{-1} due to the methyl groups, being the same band at 1370 cm^{-1} in a 1,4 structure.[13] The ^{13}C NMR spectrum of the polymer is reported in Figure 8; five main peaks at 15.67, 35.78, 40.34, 121.83, and 134.90 can be observed which were assigned as indicated on the basis of what already reported in the literature;[14] some minor peaks around the main ones, most probably due to a certain amount of stereoirregularities, can be detected. The ^1H NMR spectrum is shown in Figure 9, and it was assigned as indicated;[13,15] in particular, the signal corresponding to the methylene protons centered at 1.02 ppm is a false triplet, and this is indicative of a polymer having a 1,2 syndiotactic structure.[8] A paper concerning a complete characterization of this new crystalline polymer including X-ray and solid state ^{13}C NMR studies to determine its molecular structure will be submitted for publication soon. To our knowledge, this is the first synthesis of a crystalline *trans*-1,2 syndiotactic polypentadiene; a 1,2 polypentadiene was in fact already synthesized several years ago by Porri with the system $Co(acac)_3$−$AlEt_2Cl$ using heptane as polymerization solvent, but it was found to be amorphous.[16]

The system $CoCl_2(P^iPrPh_2)_2$−MAO gives a crystalline polymer (Figure 2c) with a melting point of 89 °C (Figure 6d) also from 1,3-hexadiene. The IR spectrum of the polymer is shown in Figure 3d. The absence of any band at 911 and 751 cm^{-1} excludes the presence of 3,4 and *cis*-1,4 units, respectively; the intense band observed at 965 cm^{-1} is instead indicative of a trans configuration of the double bond,[13] even if it does not permit one to distinguish between a *trans*-1,4 structure and a *trans*-1,2 structure. Figure 10 shows the ^{13}C NMR spectrum of the polymer consisting of six main resonances at 14.38, 25.80, 37.46, 42.21, 132.03, and 133.88 ppm; as occurred in the case of polypentadiene, some minor peaks around the main ones, most probably due to a certain amount of stereoirregularities, can be detected. The fact that this ^{13}C NMR spectrum is different from those of *cis*-1,4 isotactic,[17] *cis*-1,4 syndiotactic,[17] and especially *trans*-1,4 isotactic[18] polyhexadienes seems to suggest a 1,2 structure for the polymer under study. The formation of a 1,2 polymer having a trans structure is also in agreement with the following

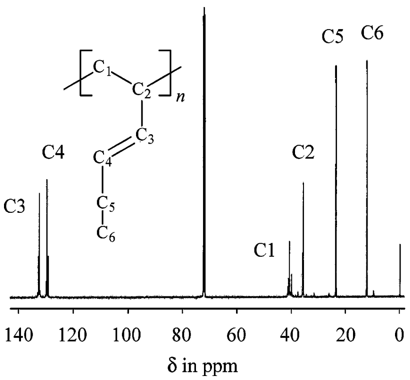

Figure 10. ^{13}C NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of the polyhexadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 3, run 3).

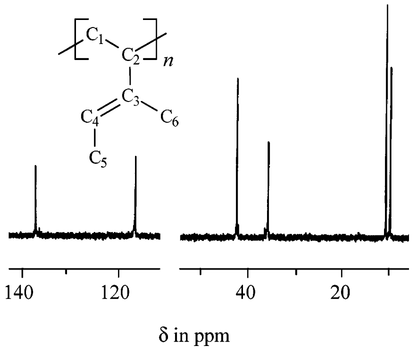

Figure 11. ^{13}C NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of the poly(3-methylpentadiene) obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 3, run 4).

experimental evidence. As reported in the Experimental Section, the monomer used for this work is a mixture of *E* and *Z* isomers, but only the *E* isomer is consumed during the polymerization, as indicated by the fact that the *Z* isomer can be quantitatively recovered at the end of the polymerization.[19] NMR and X-ray studies are in progress in order to determine the type of tacticity of the polymer; nevertheless, a syndiotactic structure appears to be the most probable one if we consider that the system $CoCl_2(P^iPrPh_2)_2$−MAO has given, as reported above, a 1,2 syndiotactic polymer from 1,3-butadiene and in particular from 1,3-pentadiene, a monomer very similar to 1,3 hexadiene.

A *trans*-1,2 polyhexadiene was never obtained before since, up to now, only three types of stereoregular polyhexadienes have been described in the literature: *cis*-1,4 isotactic, obtained with the system $Nd(OCOR)_3$−$AlEt_2Cl$−$Al(^iBu)_3$;[17] *cis*-1,4 syndiotactic, obtained with the systems $Co(acac)_3$−MAO and $Ni(acac)_2$−MAO,[17] and *trans*-1,4 isotactic obtained with the heterogeneous system VCl_3−$AlEt_3$.[18] As for the *trans*-1,2 syndiotactic polypentadiene reported above, a paper regarding a complete characterization of the polymer is in preparation.

Finally, the system $CoCl_2(P^iPrPh_2)_2$−MAO was also used for the polymerization of 3-methyl-1,3-pentadiene; a crystalline polymer (Figure 2d) having a melting point of about 79 °C (Figure 6e) was obtained. Up to now, only two stereoregular poly(3-methyl-1,3-pentadiene)s were reported in the literature: *cis*-1,4 isotactic poly(3-methylpentadiene) obtained with the system $Nd(OCOR)_3$−$AlEt_2Cl$−$Al(^iBu)_3$ [20] and *cis*-1,4 syndiotactic poly(3-methylpentadiene) obtained with the system $Ni(acac)_2$−MAO.[21] Actually also a 1,2 polymer has been recently obtained with the system $FeEt_2(bipy)_2$−MAO, but nothing has been reported on its tacticity;[22] this polymer is crystalline with a very high melting point (192 °C) and is insoluble in aliphatic and aromatic solvents also at high temperature.

The ^{13}C NMR spectrum of the poly(3-methylpentadiene) obtained with $CoCl_2(P^iPrPh_2)_2$−MAO, consisting of six main resonances at 10.15, 11.04, 35.76, 42.40, 116.65, and 137.61 ppm, is shown in Figure 11. The facts that (*i*) this ^{13}C NMR spectrum is completely different from those of the stereoregular 1,4 poly(3-methylpentadiene) previously reported[20,21] and (*ii*) in the IR spectrum (Figure 3e) no band at 911 cm^{-1}, typical of a 3,4 structure, is observed, while a very intense band at 823 cm^{-1} can be detected, seem to indicate that the polymer has a 1,2 structure. On the other hand, also the ppm values of the resonances in the ^{13}C NMR spectrum (Figure 11), accordingly to what already reported in the literature for other vinylic polydienes, is in agreement with a 1,2 structure.[7c,e−g,11,14,23]

As reported in the Experimental Section, the 3-methyl-1,3-pentadiene used in the polymerization run is a mixture of *E* and *Z* isomers; the fact that, as occurred in the polymerization of 1,3-hexadiene, the *Z* isomer can be quantitatively recovered at the end of polymerization[19] seems to indicate that only the *E* isomer is polymerized and that indeed the polymer obtained has a *trans*-1,2 structure.

We have reported above that a 1,2 poly(3-methylpentadiene) has been recently obtained by Porri with the system $FeEt_2(bipy)_2$−MAO;[22] we have synthesized this polymer in our laboratory by using an analogous iron system ($FeCl_2(bipy)_2$−MAO)[24] and have compared it with the 1,2 poly(3-methylpentadiene) obtained with $CoCl_2(P^iPrPh_2)_2$−MAO. The two polymers have different melting points (Figure 6e,f), IR spectra (Figure 3e,f) and X-ray powder spectra (Figure 2d,e). Since we have found that also in the polymerization of 3-methylpentadiene with iron catalysts only the *E* isomer is consumed, it follows that the two polymers should have most probably a different tacticity. Work is in progress, in particular through NMR (in solution and in the solid state) and X-ray studies to assign to both the poly(3-methylpentadiene)s the correct microstructure and tacticity.

The results reported above have also some mechanistic implications. It has been previously reported that the system $CpTiCl_3$−MAO polymerizes several types of 1,3-dienes, giving polymers with different structure from the different monomers.[25] This phenomenon was interpreted by assuming that the presence of substituents on C1 or C3 of the allylic unit may influence the reactivity of these two positions favoring the formation of a 1,2 or a 1,4 unit, respectively. Something analogous is observed in the polymerization of butadiene, isoprene, 1,3-pentadiene, 1,3-hexadiene, and 3-methyl-1,3-pentadiene with the system $CoCl_2(P^iPrPh_2)_2$−MAO; exclusively 1,2 units are present in the polymers obtained from 1,3-pentadiene, 1,3-hexadiene, and 3-methyl-1,3-pentadiene, while polymers containing a certain amount of *cis*-1,4 units are obtained from butadiene (15−20%) and isoprene (43%). These results are the expected ones according to the interpretation reported in our previous paper,[25] confirming indeed its validity. The allylic units formed during the polymerization of the above monomers are those shown in Figure 12. It can be observed that in the case of pentadiene, hexadiene, and 3-meth-

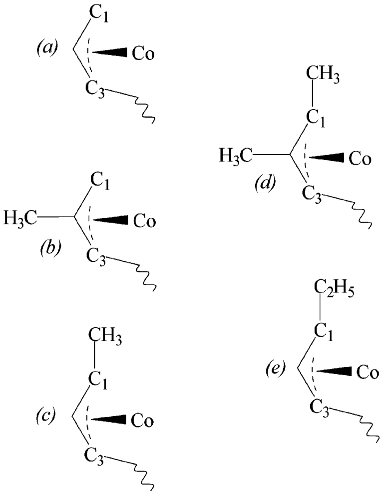

Figure 12. Allyl units formed in the polymerization of (a) butadiene; (b) isoprene; (c) *E*-1,3-pentadiene; (d) 3-methyl-1,3-pentadiene; (e) 1,3-hexadiene with the system $CoCl_2(P^iPrPh_2)_2$–MAO.

ylpentadiene, the C1 position, due to the presence of an alkyl substituent, is more hindered and consequently less reactive with respect to the same position in the allylic unit formed in the case of butadiene or isoprene. It follows that the formation of 1,4 units (insertion of the new monomer at C1) is more probable in the polymerization of butadiene and isoprene than in the polymerization of 1,3-pentadiene, 1,3-hexadiene, and 3-methyl-1,3-pentadiene.

Conclusions

The new cobalt phosphine complex $CoCl_2(P^iPrPh_2)_2$ has been synthesized and its molecular structure determined by X-ray diffraction method. The complex associated with MAO was found to be one of the most active catalysts for the preparation of 1,2 syndiotactic polybutadiene, one of the two diene polymers of industrial interest, the other one being *cis*-1,4 polybutadiene.

It was also able to polymerize substituted butadienes such as isoprene, 1,3-pentadiene, 1,3-hexadiene, and 3-methyl-1,3-pentadiene, giving in some cases new polymers never obtained before. A preliminary characterization of these polymers has been carried out; nevertheless, further work is in progress in order to assign them the correct microstucture and tacticity, and results on this topic will be published soon.

Finally, the results obtained have permitted us to confirm what is already reported regarding the influence of the monomer structure on the polymerization chemoselectivity.[25]

Experimental Section

Materials and Methods. Cobalt(II) chloride anhydrous (Strem, >99% pure), isopropyldiphenylphosphine (Aldrich, 97% pure), and MAO (Crompton, 10 wt% solution in toluene) were used as received. $FeCl_2(bipy)_2$ was prepared as reported in the literature.[26] Ethyl alcohol (Carlo Erba, 96°) was degassed under vacuum then by bubbling dry nitrogen 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 nitrogen; toluene (Carlo Erba, 99.5% pure) was refluxed over Na for ca. 8 h then distilled and stored over molecular sieves under dry nitrogen. Isoprene (Fluka, ≥ 99.5% pure), *E*-1,3-pentadiene (Fluka, ≥ 96% pure), 1,3-hexadiene (Aldrich, 95% pure, mixture of *Z* and *E* isomers), and 3-methyl-1,3-pentadiene (Aldrich, 98% pure, mixture of *Z* and *E* isomers) were refluxed over calcium hydride for ca. 3 h then distilled trap-to-trap and stored under dry nitrogen. 1,3-Butadiene (Air Liquide, > 99.5% pure) was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves, and condensed into the reactor which had been precooled to −20 °C.

Table 4. Crystal Data, Details of Data Collection, and Results of the Refinement for $CoCl_2(P^iPrPh_2)_2$

formula	$C_{30}H_{34}Cl_2CoP_2$
M_r	586.34
crystal system	monoclinic
space group	$P2_1/n$
Z	4
D_{calc}, g cm^{-3}	1.291
A, Å	11.082(2)
B, Å	16.191(3)
C, Å	17.047(4)
β, °	99.607(10)
V, Å^3	3015.9(11)
crystal size, mm	0.34 × 0.22 × 0.20
color, habit	light blue, rhombic prism
μ , mm^{-1}	0.869
radiation	Mo K_α
T, K	293(2)
$2\theta_{max}$, °	58.00
h, k, l ranges	$-15 \rightarrow 15$; $-22 \rightarrow 22$; $-23 \rightarrow 23$
intensity decay, %	0.00
absorption correction	multiscan (Bruker SADABS)
T_{min}, T_{max}	0.867,1.000
measured reflections	40775
R_{int}	0.0376
independent reflections	8013
reflections with $I > 2\sigma(I)$	6352
no. of parameters	316
$R(F^2)$, $wR(F^2)$	0.0652, 0.1101
$R[F^2 > 2\sigma(F^2)]$, $wR[F^2 > 2\sigma(F^2)]$	0.0493, 0.1034
gof	1.116
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.411, −0.256

Synthesis of $CoCl_2(P^iPrPh_2)_2$. Isopropyldiphenyphosphine (4.09 g, 17.9 mmol) as ethanol solution (20 mL) was added under stirring to a solution of $CoCl_2$ (0.97 g, 7.5 mmol) in ethyl alcohol (50 mL). The reaction was stirred at room temperature for ca. 24 h; at the end, a blue−turquoise suspension is formed. The solvent was partially removed under vacuum then the precipitate was filtered off, washed with small amounts of ethanol (3 × 10 mL) and pentane (2 × 10 mL), and then dried at room temperature under vacuum. The blue solid obtained was then extracted continuously with boiling pentane; crystals of $CoCl_2(P^iPrPh_2)_2$ were formed directly on the bottom of the Schlenk tube during the extraction, and further crops of crystals were obtained by cooling the supernatant pentane solution at −30 °C. Yield: 3.59 g (81.6% based on $CoCl_2$). Anal. Calcd. for $C_{30}H_{34}CoCl_2P_2$: Co, 10.05; Cl, 12.09; P, 10.56. Found: Co, 9.9; Cl, 12.2; P, 11.1. IR (KBr) ν (cm^{-1}): 3078m, 3051m, 2956s, 2929m, 2866m, 1484s, 1461m, 1436s, 1385m, 1366w, 1317w, 1290w, 1245w, 1188m, 1159w, 1102s, 1073w, 1037m, 998w, 880w, 738s, 691s, 653w, 626m, 519s, 490m, 460m.

X-Ray Structure Determination of $CoCl_2(P^iPrPh_2)_2$. A summary of the experimental details is reported in Table 4. The crystal used for the data collection was 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 multiscan were obtained by SADABS.[27] The structure was solved by SIR92[28] and refined on F^2 by full-matrix least-squares using SHELX97.[29] For molecular graphics the program ORTEP-III [30] was used.

Polymerization. All operations were carried out under an atmosphere of dry nitrogen. 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. MAO and the cobalt compound were then added, as toluene solutions, in 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 a vacuum at room temperature. The polymerizations of the other monomers (isoprene, 1,3-pentadiene, 1,3-hexadiene, and 3-methyl-1,3-pentadiene) were carried out in a similar way. The polymerization of 3-methyl-1,3-pentadiene with $FeCl_2(bipy)_2$−MAO was carried out in a similar way; the polymerization conditions are reported in Table 3.

Polymer Characterization. ^{13}C and ^1H NMR measurements were performed with a Bruker AM 270 instrument. The spectra were obtained in $C_2D_2Cl_4$ at 103 °C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was about 10 wt%. The infrared spectra were recorded on a Bruker IFS 48 instrument; the polymer spectra were obtained by 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.

Differential scanning calorimetry (DSC) scans were carried out on Perkin-Elmer Pyris 1 instrument: typically, ca. 5 mg of polymer was analyzed in each run, while the scan speed was 20 °C/min under nitrogen atmosphere.

The molecular weight averages and 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 temperature. The calibration of the GPC system was constructed by 18 narrow MWD polystyrene standards with the molar mass ranging from 162 to 3.3×10^6 g/mol.

The wide-angle X-ray diffraction (WAXD) data were obtained at 20 °C using a Siemens D-500 diffractometer equipped with a Siemens FK 60-10 2000 W tube (Cu Kα radiation, $\lambda = 0.154$ nm). The operating voltage and current were 40 kV and 40 mA, respectively. The data were collected from 5 to 35 $2\theta°$ at 0.02 $2\theta°$ intervals.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, bond distances, and angles for $CoCl_2(P^iPrPh_2)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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