

# Synthesis, structure, and butadiene polymerization behavior of alkylphosphine cobalt(II) complexes

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## Abstract

The synthesis, characterization and behavior in polymerization of 1,3-butadiene of some cobalt(II) phosphine complexes ( $\text{CoCl}_2(\text{PEt}_3)_2$ ,  $\text{CoCl}_2(\text{P}^n\text{Pr}_3)_2$ ,  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$ ,  $\text{CoCl}_2(\text{P}^t\text{Bu}_2\text{H})_2$ ,  $\text{CoCl}_2(\text{P}^t\text{Bu}_2\text{Me})_2$ ,  $\text{CoCl}_2(\text{PCyp}_3)_2$ ,  $\text{CoCl}_2(\text{PCy}_3)_2$ ; Et = ethyl, <sup>n</sup>Pr = *normal*-propyl, Cy = cyclohexyl, <sup>t</sup>Bu = *tert*-butyl, Cyp = cyclopentyl) are described. The X-ray diffraction studies of  $\text{CoCl}_2(\text{PCy}_3)_2$  and  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$  are reported. Treatment of these complexes with methylaluminoxane (MAO) leads to highly active butadiene polymerization catalysts; polymers having different microstructure have been obtained depending on the type of phosphine ligand bonded to the cobalt atom. An interpretation for this particular behavior, based on the 1,3-dienes polymerization mechanism previously proposed, is given.

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**Keywords:** Cobalt phosphine complexes; X-ray structure; Cobalt catalysts; Butadiene polymerization; Polybutadiene

## 1. Introduction

Cobalt catalysts play a very important role in the field of butadiene polymerization since, depending on the catalytic formulation, they can give *cis*-1,4 polybutadiene or 1,2 syndiotactic polybutadiene, the only two diene polymers of industrial interest and industrially produced [1].

For instance, the system  $\text{Co}(\text{acac})_3\text{-AlEt}_2\text{Cl-H}_2\text{O}$  gives a highly *cis*-1,4 polybutadiene (~97%) [2]; equibinary *cis*-1,4/1,2 polybutadiene is obtained with the system  $\text{Co}(\text{acac})_3\text{-AlEt}_3\text{-H}_2\text{O}$  [3]; when  $\text{CS}_2$  is added to this system 1,2 syndiotactic polybutadiene is obtained [4]. Highly syndiotactic 1,2 polybutadiene is also prepared with the system  $(\text{C}_4\text{H}_6)(\eta^5\text{-C}_5\text{H}_8)\text{Co-CS}_2$  [5], but also the cobalt complex alone is able to give highly syndiotactic polybutadiene [6].

Moreover, it has been reported that the system  $\text{CoBr}_2(\text{PPh}_3)_2\text{-MAO}$  gives from butadiene a polymer with a mixed *cis*-1,4/1,2 structure [7] in which the *cis*-1,4 and 1,2

units are randomly distributed along the polymer chain [8]. A highly *cis*-1,4 polybutadiene was obtained with  $\text{CoCl}_2\text{-MAO}$  [9], while a predominantly 1,2 syndiotactic polymer was obtained with the same system in presence of  $\text{PPh}_3$  [10]. These latter results seem to suggest that the presence of a ligand bonded to the metal strongly affects the catalyst chemoselectivity and consequently the polymer microstructure. For a better understanding of this behavior we have prepared several cobalt(II) phosphine complexes; the X-ray structures of some of these complexes have been determined, after which they have been used in combination with MAO for polymerizing butadiene. The most significant results obtained are reported in this paper.

## 2. Experimental

### 2.1. Materials and methods

Triethylphosphine ( $\text{PEt}_3$ ) (Strem, 99% pure), tri-*normal*-propylphosphine ( $\text{P}^n\text{Pr}_3$ ) (Strem, min. 95% pure), dicy-

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clohexylphosphine ( $\text{PCy}_2\text{H}$ ) (Strem, 98% pure), di-*tert*-butylphosphine ( $\text{P}^t\text{Bu}_2\text{H}$ ) (Strem, >95% pure), di-*tert*-butylmethylphosphine ( $\text{P}^t\text{Bu}_2\text{Me}$ ) (Strem, >98% pure), tricyclopentylphosphine ( $\text{PCyp}_3$ ) (Strem, >97% pure), tricyclohexylphosphine ( $\text{PCy}_3$ ) (Strem, 97% pure), anhydrous cobalt dichloride (Aldrich, 99.9% pure) and 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 prior to each run, dried by passing through a column packed with molecular sieves and condensed into the reactor which had been precooled to  $-20^\circ\text{C}$ . All the phosphine cobalt complexes were synthesized as indicated below, following a general experimental procedure reported in [11]. The elemental analyses of the cobalt complexes were performed by the analytical laboratories of Polimeri Europa-Centro Ricerche Novara-“Istituto Guido Donegani”; infrared spectra were recorded as KBr disks with a Bruker IFS 48 instrument.

## 2.2. Synthesis of $\text{CoCl}_2(\text{PEt}_3)_2$

Triethylphosphine (2 mL, 13.9 mmol) was added to a solution of  $\text{CoCl}_2$  (0.60 g, 5.53 mmol) in ethyl alcohol (50 mL). The solution immediately became dark blue. The reaction was kept under stirring for 20 h at room temperature, then the solvent was removed under vacuum; a large amount of blue needles were formed while removing the solvent. The blue crystalline residue was washed with small amounts of pentane at low temperature and dried again under vacuum; then it was extracted in continuous with boiling pentane for about 24 h. At the end of the extraction a crystalline blue product was formed; the supernatant solution was removed and further crops of crystals were obtained by cooling it at  $-30^\circ\text{C}$ . Yield: 1.72 g (64.2% based on  $\text{CoCl}_2$ ).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{30}\text{CoCl}_2\text{P}_2$ : Co, 16.10; Cl, 19.36; P, 16.92. Found: Co, 16.2; Cl, 19.5; P, 17.0.

Spectroscopic data: IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 2970s, 2938m, 2880m, 1459s, 1417s, 1383m, 1259w, 1121w, 1038s, 1013w, 771s, 758s, 736m, 699w, 623w.

## 2.3. Synthesis of $\text{CoCl}_2(\text{P}^n\text{Pr}_3)_2$

Tri-*normal*-propylphosphine (4.6 mL, 23.1 mmol) was added under stirring to a solution of  $\text{CoCl}_2$  (1.20 g, 9.22 mmol) in ethyl alcohol (50 mL). The solution became immediately dark blue; after 20 h under stirring the solvent was removed under vacuum at room temperature. The blue residue was washed with small amounts of pentane at low temperature and dried again under vacuum; then it

was extracted in continuous with boiling pentane for about 24 h. At the end of the extraction a crystalline blue product was formed; the supernatant solution was removed and further crops of crystals were obtained by cooling it at  $-30^\circ\text{C}$ . Yield: 3.82 g (92% based on  $\text{CoCl}_2$ ). Anal. Calcd. for  $\text{C}_{18}\text{H}_{42}\text{CoCl}_2\text{P}_2$ : Co, 13.09; Cl, 15.75; P, 13.76. Found: Co, 13.3; Cl, 16.1; P, 13.8.

Spectroscopic data: IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 2961s, 2873s, 1462s, 1417s, 1378m, 1223m, 1088s, 1050m, 905w, 850m, 761s, 724m, 645w, 434w.

## 2.4. Synthesis of $\text{CoCl}_2(\text{PCy}_2\text{H})_2$

To a solution of  $\text{CoCl}_2$  (0.81 g, 6.2 mmol) in ethyl alcohol, dicyclohexylphosphine (3.69 g, 18.6 mmol) was added under stirring. A blue precipitate is immediately formed; the suspension was kept under vigorous stirring for 24 h, then filtered. The blue solid on the filter was washed with ethyl alcohol ( $3 \times 10$  mL) and pentane ( $2 \times 10$  mL), then dried under vacuum. It was then extracted in continuous with boiling pentane for several days; at the end a crystalline product is formed on the bottom of the Schlenk flask containing the extracting solution and further crops of crystals can be isolated by removing the supernatant pentane solution and cooling it at  $-30^\circ\text{C}$ . Yield: 2.74 g (83.9% based on  $\text{CoCl}_2$ ).

Anal. Calcd. for  $\text{C}_{24}\text{H}_{46}\text{CoCl}_2\text{P}_2$ : Co, 11.20; Cl, 13.47; P, 11.77. Found: Co, 11.1; Cl, 13.4; P, 11.9.

Spectroscopic data: IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 2917s, 2847s, 1450s, 1347w, 1327w, 1302w, 1264m, 1194m, 1182m, 1112m, 1074w, 1002m, 917w, 891m, 867w, 853m, 822m, 806s, 713w, 511w.

## 2.5. Synthesis of $\text{CoCl}_2(\text{P}^t\text{Bu}_2\text{H})_2$

Di-*tert*-butylphosphine (1.62 g, 11.1 mmol) was added to a solution of  $\text{CoCl}_2$  (0.48 g, 3.7 mmol) in ethyl alcohol (20 mL). An extremely dense suspension was immediately formed, which was kept under vigorous stirring for ca. 24 h, then filtered. A blue residue is obtained, which was washed with ethyl alcohol ( $3 \times 10$  mL) and pentane ( $2 \times 10$  mL), dried under vacuum and then extracted in continuous with boiling pentane for a few days. Crystals of the complex are formed directly during the extraction and further crops of crystals are obtained by removing the supernatant pentane solution and cooling it at  $-30^\circ\text{C}$ . Yield: 1 g (64% based on  $\text{CoCl}_2$ ).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{38}\text{CoCl}_2\text{P}_2$ : Co, 13.96; Cl, 16.79; P, 14.67. Found: Co, 13.8; Cl, 17.1; P, 14.9.

Spectroscopic data: IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 3002w, 2981m, 2955s, 2902m, 2868m, 1471s, 1394w, 1370s, 1208w, 1180s, 1141w, 1110w, 1030s, 962w, 944m, 920w, 885m, 820m, 804m, 616m, 584w, 464m, 409w.

## 2.6. Synthesis of $\text{CoCl}_2(\text{P}^t\text{Bu}_2\text{Me})_2$

To a solution of  $\text{CoCl}_2$  (0.37 g, 2.8 mmol) in ethyl alcohol (25 mL) a solution of di-*tert*-butylmethylphosphine (1.35 g,

8.4 mmol) in ethyl alcohol (10 mL) was added. A blue suspension was immediately formed; it was kept under stirring for 24 h, then filtered. The blue residue on the filter was washed with small amounts of ethyl alcohol and pentane, then dried under vacuum. Crystals of  $\text{CoCl}_2(\text{P}'\text{Bu}_2\text{Me})_2$  were obtained by extraction of the blue solid in continuous with boiling pentane for some days; the crystals were formed directly during the extraction and further crops of crystals were obtained by removing the pentane solution and cooling it at  $-30^\circ\text{C}$ . Yield: 0.88 g (70.3% based on  $\text{CoCl}_2$ ).

Anal. Calcd. for  $\text{C}_{18}\text{H}_{42}\text{CoCl}_2\text{P}_2$ : Co, 13.09; Cl, 15.75; P, 13.76. Found: Co, 13.7; Cl, 16.3; P, 13.5.

Spectroscopic data: IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 2963s, 2949s, 2905m, 2873m, 1475s, 1396m, 1372s, 1304s, 1182w, 1127s, 1101s, 1047m, 1025m, 943m, 886s, 818s, 759m, 726w, 641m, 485w, 471w, 455m, 414w.

### 2.7. Synthesis of $\text{CoCl}_2(\text{PCy}_3)_2$

Tricyclopentylphosphine (3.0 g, 12.5 mmol) was added to a solution of  $\text{CoCl}_2$  (0.64 g, 4.9 mmol) in ethyl alcohol (40 mL). A blue suspension was rapidly formed: it was kept under stirring for 24 h, then filtered. The blue residue was washed with ethyl alcohol and pentane, dried under vacuum, then extracted in continuous with boiling pentane for a few days. A crystalline product is formed directly during the extraction, while further crops of crystals are obtained from the supernatant by concentrating and cooling at low temperature. Yield: 2.44 g (82.1% based on  $\text{CoCl}_2$ ).

Anal. Calcd. for  $\text{C}_{30}\text{H}_{54}\text{CoCl}_2\text{P}_2$ : Co, 9.72; Cl, 11.69; P, 10.21. Found: Co, 9.6; Cl, 11.7; P, 10.4.

Spectroscopic data: IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 2956s, 2911m, 2867s, 1449s, 1372w, 1301m, 1262m, 1238m, 1128s, 910w, 852m, 536m, 523m, 484w.

### 2.8. Synthesis of $\text{CoCl}_2(\text{PCy}_3)_2$

Tricyclohexylphosphine (6.24 g, 22.2 mmol) was added to a solution of  $\text{CoCl}_2$  (1.16 g, 8.9 mmol) in ethyl alcohol (50 mL). After a few minutes a blue suspension was formed; it was kept under stirring for 24 h, then filtered. The residue on the filter was washed with ethanol ( $3 \times 10$  mL), then dried under vacuum. A crystalline product was obtained by extracting the blue residue in continuous with boiling pentane; blue crystals were formed directly during the extraction. The supernatant was removed and further crops of crystals were obtained by cooling it at  $-30^\circ\text{C}$ . Yield: 5.51 g (89.6% based on  $\text{CoCl}_2$ ).

Anal. Calcd. for  $\text{C}_{36}\text{H}_{66}\text{CoCl}_2\text{P}_2$ : Co, 8.53; Cl, 10.27; P, 8.79. Found: Co, 8.6; Cl, 10.5; P, 8.9.

Spectroscopic data: IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ) 2928s, 2849s, 1447s, 1345w, 1329w, 1301w, 1268m, 1199w, 1176m, 1128w, 1113m, 1004m, 917w, 888m, 850m, 818w, 738w, 515m, 488w.

Table 1  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$

Co—Cl	2.2182(6)
Co—P	2.3942(6)
P—C1	1.8370(16)
P—C7	1.858(3), 1.804(12)
Cl—Co—Cl'	109.81(3)
P—Co—P'	105.87(3)
Cl—Co—P	109.69(2)
Cl—P—C7	104.73(10), 118.1(4)

### 2.9. X-ray crystallographic studies

A summary of the experimental details concerning the X-ray diffraction study of  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$  and  $\text{CoCl}_2(\text{PCy}_3)_2$  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 multiscan were obtained by SADABS [12]. The structures were solved by SIR92 [13] and refined on  $F^2$  by full-matrix least-squares using SHELX97 [14]. The program ORTEP-III [15] was used for molecular graphics.

### 2.10. 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  $-20^\circ\text{C}$ , 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 solu-

Table 2  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $\text{CoCl}_2(\text{PCy}_3)_2$

Co—Cl1	2.2319(6)
Co—Cl2	2.2389(6)
Co—P1	2.4375(6)
Co—P2	2.4345(6)
P1—C1	1.848(2)
P1—C7	1.854(2)
P1—C13	1.857(2)
P2—C19	1.881(4), 1.882(4)
P2—C25	1.852(2)
P2—C31	1.851(2)
Cl1—Co—Cl2	112.69(3)
P1—Co—P2	125.61(2)
Cl1—Co—P1	110.76(2)
Cl1—Co—P2	98.78(2)
Cl2—Co—P1	99.14(2)
Cl2—Co—P2	110.31(2)
C1—P1—C7	110.68(10)
C1—P1—C13	103.04(9)
C7—P1—C13	105.60(10)
C19—P2—C25	118.7(2), 95.8(2)
C19—P2—C31	96.7(2), 112.6(2)
C25—P2—C31	104.20(10)

Table 3  
Polymerization of butadiene with different cobalt catalysts

Run	Catalyst	Polymerization <sup>a</sup>				Polymer			
		Co-compound	$\theta^b$ (°)	Time (min)	Conv (%)	$N^c$ (min <sup>-1</sup> )	<i>cis</i> -1,4 <sup>d</sup> (%)	1,2 <sup>d</sup> (%)	Mw (g × mol <sup>-1</sup> )
1	CoCl <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub>	132	30	74.8	129	39.9	60.1		
2	CoCl <sub>2</sub> (P <sup><i>ν</i></sup> Pr <sub>3</sub> ) <sub>2</sub>	132	35	85.5	127	38.2	61.8		
3	CoCl <sub>2</sub> (PCy <sub>2</sub> H) <sub>2</sub>	143	30	70.8	122	51.0	49.0	280000	1.9
4	CoCl <sub>2</sub> (P <sup><i>t</i></sup> Bu <sub>2</sub> H) <sub>2</sub>	150	35	60.4	89	59.0	41.0	275000	2.0
5	CoCl <sub>2</sub> (P <sup><i>t</i></sup> Bu <sub>2</sub> Me) <sub>2</sub>	161	40	59.0	76	94.0	6.0	260000	1.8
6	CoCl <sub>2</sub> (PCyp <sub>3</sub> ) <sub>2</sub>	39	39	56.4	85	73.6	26.4	245000	2.0
7	CoCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub>	170	32	44.4	72	77.4	22.6	250000	2.1

<sup>a</sup> Polymerization conditions: butadiene, 2 mL; toluene, 16 mL; Al/Co = 1000; moles of Co,  $5 \times 10^{-6}$ ; +20 °C.

<sup>b</sup> Phosphine cone angle, as reported by Tolman (Ref. [21]).

<sup>c</sup> *N*: moles of butadiene polymerized per mol of Co per minute.

<sup>d</sup> Determined by <sup>1</sup>H NMR, as shown in Fig. 3. *Trans*-1,4 units are almost negligible, as indicated by the IR spectra of the polymers.

tions, 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.

#### 2.10.1. Polymer characterization

<sup>13</sup>C and <sup>1</sup>H NMR measurements were performed with a Bruker AM 270 instrument. The spectra were obtained in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 103 °C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was

about 10 wt.%. The infrared spectra of the polymers 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.

MW and MWD were determined by GPC analysis using the universal calibration method. The GPC system was composed by a Agilent 1100 pump, a detector IR Agilent 1100 and PL Mixed-A columns; tetrahydrofuran (1 mL/min) was used as solvent at 25 °C.

Table 4  
Crystal data, details of data collection and results of the refinement for CoCl<sub>2</sub>(PCy<sub>2</sub>H)<sub>2</sub> and CoCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>

Compound	CoCl <sub>2</sub> (PCy <sub>2</sub> H) <sub>2</sub>	CoCl <sub>2</sub> (PCy <sub>3</sub> ) <sub>2</sub>
Formula	C <sub>24</sub> H <sub>46</sub> Cl <sub>2</sub> CoP <sub>2</sub>	C <sub>36</sub> H <sub>66</sub> Cl <sub>2</sub> CoP <sub>2</sub>
<i>M<sub>r</sub></i>	526.38	690.66
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2/c</i>	<i>P2<sub>1</sub>/n</i>
<i>Z</i>	2	4
<i>D<sub>calc</sub></i> (g cm <sup>-3</sup> )	1.271	1.206
<i>a</i> (Å)	11.941(2)	10.4845(10)
<i>b</i> (Å)	5.7615(12)	15.8069(15)
<i>c</i> (Å)	20.296(4)	22.973(2)
$\beta$ (°)	99.96(3)	91.903(10)
<i>V</i> (Å <sup>3</sup> )	1375.3(5)	3805.1(6)
Crystal size	0.35 mm × 0.25 mm × 0.10 mm	0.30 mm × 0.20 mm × 0.05 mm
Colour, habit	Light blue, Rectangular prism	Light blue, Rectangular prism
$\mu$ (mm <sup>-1</sup> )	0.944	0.698
Radiation	Mo K $\alpha$	Mo K $\alpha$
<i>T</i> (K)	293(2)	293(2)
$2\theta_{\max}$ (°)	68.6	58.0
<i>h, k, l</i> ranges	−18 → 18; −9 → 9; −31 → 31	−14 → 14; −21 → 21; −31 → 31
Intensity decay (%)	0.00	0.00
Absorption correction	Multi-scan (Bruker SADABS)	Multi-scan (Bruker SADABS)
<i>T<sub>min</sub>, T<sub>max</sub></i>	0.876, 1.000	0.926, 1.000
Measured reflections	20912	79767
<i>R<sub>int</sub></i>	0.0250	0.0420
Independent reflections	5448	10103
Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	4074	7881
No. of parameters, restraints	187, 0	416, 12
<i>R</i> ( <i>F</i> <sup>2</sup> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0583, 0.1157	0.0608, 0.1251
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.0403, 0.1065	0.0453, 0.1151
Goodness-of-fit	1.041	1.050
( $\Delta$ / $\sigma$ ) <sub>max</sub>	0.001	0.002
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e $\text{\AA}^{-3}$ )	0.645, −0.238	0.631, −0.291

Polybutadiene microstructure was determined as reported in [16].

### 3. Results and discussion

#### 3.1. Synthesis and characterization of the cobalt phosphine complexes

The cobalt phosphine complexes were prepared following the experimental procedure already described in the literature for this type of compounds [11]. The following phosphines were used: triethylphosphine ( $\text{PEt}_3$ ), tri-*normal*-propylphosphine ( $\text{P}^n\text{Pr}_3$ ), dicyclohexylphosphine ( $\text{PCy}_2\text{H}$ ), di-*tert*-butylphosphine ( $\text{P}^t\text{Bu}_2\text{H}$ ), di-*tert*-butylmethylphosphine ( $\text{P}^t\text{Bu}_2\text{Me}$ ), tricyclopentylphosphine ( $\text{PCyp}_3$ ) and tricyclohexylphosphine ( $\text{PCy}_3$ ).

Anhydrous cobalt dichloride was dissolved in ethanol, then the phosphine (P/Co molar ratio = 2.5–3) was added; depending on the type of phosphine, completely homogeneous blue solutions or heterogeneous blue suspensions were obtained. In case of homogeneous solution, the solvent was removed under vacuum and a crystalline product was obtained by continuous extraction of the residue with boiling pentane; in case of heterogeneous suspension, the precipitate was filtered off and then again a crystalline product was obtained by continuous extraction of the residue with boiling pentane. A more detailed description of the cobalt complexes synthesis is reported in Section 2.

Single crystals suitable for X-ray structure determination were obtained for the complexes  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$  and  $\text{CoCl}_2(\text{PCy}_3)_2$  by recrystallization from pentane solution at low temperature ( $-30^\circ\text{C}$ ). In the case of  $\text{CoCl}_2(\text{PCyp}_3)_2$ , several attempts of recrystallization (from pentane, toluene or pentane/toluene mixed solutions) yielded seemingly good prismatic crystals, which however X-ray analysis proved to be twinned. The large disorder probably affecting the cyclopentyl groups prevented in all cases to solve structure for the different twin components. For the other complexes, only microcrystalline compounds have been obtained. Attempts to precipitate suitable monocrystals are in progress.

The molecular structures of  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$  and  $\text{CoCl}_2(\text{PCy}_3)_2$  are shown in Figs. 1 and 2, respectively, and selected bond lengths and angles are reported in Tables 1 and 2. The effect of the increased dimensions of the phosphine groups on going from  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$  to  $\text{CoCl}_2(\text{PCy}_3)_2$  is clearly visible by comparing corresponding Co–Cl and especially Co–P bond lengths. In both cases they undergo an increase, by 0.0172(6) and 0.0418(6) Å on average, respectively, on going from the former to the latter complex, indicating an electronic rearrangement within the core of the two complexes. The increased sterical demands are also responsible of an enlargement by  $19.74(3)^\circ$  in the P–Co–P bond angle. The comparison between corresponding P–C bond lengths in the two complexes appears to be less significant in terms of experimental error, owing

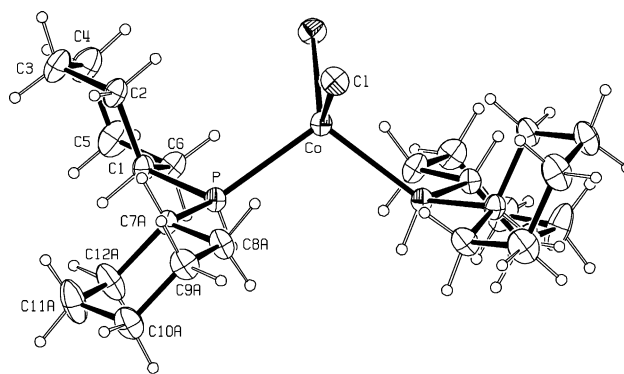


Fig. 1. ORTEP plot [15] of  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$  with atom numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

to structural disorder which affects one cyclohexyl ring in both structures, the C7–C12 one in  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$  and the C19–C24 ring in  $\text{CoCl}_2(\text{PCy}_3)_2$  (in Figs. 1 and 2 only one of the two alternative conformations is shown). However, by comparing the weighted mean value of all the P–C distances in  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$ , 1.838(3) Å, and in  $\text{CoCl}_2(\text{PCy}_3)_2$ , 1.855(4) Å, we observe also in this case a small lengthening associated to the increased bulkiness of the substituents. In all cases the cyclohexyl groups are in the chair conformation, with bond lengths and angles having values similar to those normally observed for this kind of aliphatic ring.

The metal–phosphorous (M–P) distances in both  $\text{CoCl}_2(\text{PCy}_2\text{H})_2$  and  $\text{CoCl}_2(\text{PCy}_3)_2$  complexes appear to be particularly long if compared with those observed in the same complexes of other transition metals whose structure is reported in literature. In  $\text{NiCl}_2(\text{PCy}_2\text{H})_2$  [17], the two M–P distances measure 2.1392 and 2.1618 Å and in  $\text{NiCl}_2(\text{PCy}_3)_2$  [18],  $\text{PdCl}_2(\text{PCy}_3)_2$  [19] and  $\text{PtCl}_2(\text{PCy}_3)_2$  [20] complexes, the unique M–P bond lengths are 2.2779, 2.3628 and 2.3372 Å, respectively. On the other hand, the Co–Cl distances are fairly similar to the Ni–Cl distances in the complexes with  $\text{PCy}_2\text{H}$  [17] (2.189 and 2.203 Å) and  $\text{PCy}_3$  [18] (2.1880 Å) ligands, and shorter than the Pd–Cl

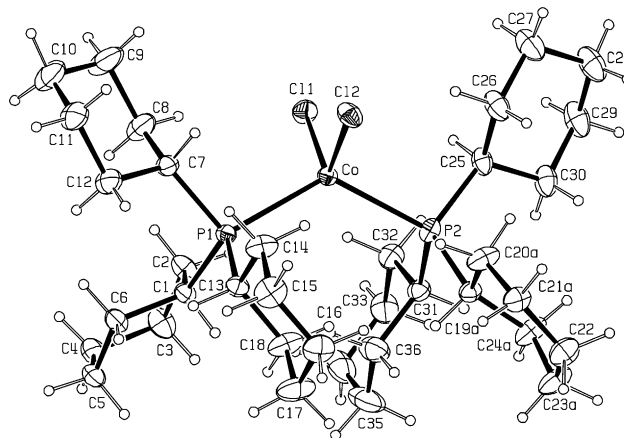


Fig. 2. ORTEP plot [15] of  $\text{CoCl}_2(\text{PCy}_3)_2$  with atom numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.



[19] and Pt–Cl [20] bond lengths (2.3011 and 2.3167 Å, respectively), as expected.

### 3.2. Polymerization of 1,3-butadiene

The results obtained in the polymerization of butadiene with the systems prepared by combining MAO with the different cobalt phosphine complexes are reported in Table 3 and can be summarized as follows.

Catalysts based on cobalt alkyl-phosphine complexes give from butadiene polymers having different structure (*cis*-1,4; mixed *cis*-1,4/1,2; predominantly 1,2) depending on the type of ligand. The *cis*-1,4 content seems to increase with increasing the ligand steric hindrance (catalysts using cyclic phosphines, PCy<sub>3</sub> and PCyp<sub>3</sub>, make an exception to this rule, even if they too give a predominantly *cis*-1,4 polybutadiene). In general, a predominantly *cis*-1,4 polymer is obtained with catalysts using more hindered ligands ( $\theta \geq 160^\circ$ ;  $\theta$  is the phosphine cone angle as reported by Tolman [21]) (Table 3, runs 5–7), while polybutadienes with a predominantly 1,2 structure or mixed *cis*-1,4/1,2 structure are obtained in the case of less hindered phosphines (Table 3, runs 1–4). When polybutadienes with a mixed structure are obtained, the *cis*-1,4 and 1,2 units are randomly distributed along the polymer chain, as indicated by the fact that polymers fractionation with different solvents always give polymeric fractions having almost the same structure as the crude polymer; it was never possible to isolate polymer fractions having a predominantly *cis*-1,4 or 1,2 structure. This result confirms what already reported in the literature: a random distribution of the different butadiene units (*cis*-1,4 and 1,2) was also observed by Soga in the polymerization of butadiene with the system CoBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>-MAO [8]. The <sup>1</sup>H NMR spectra of some of the polymers of Table 3, from which the *cis*-1,4/1,2 content (trans units are almost negligible as indicated by the IR spectra of the polymers in which the band at 967 cm<sup>-1</sup> is extremely low) can be determined as reported, are shown in Fig. 3.

The type of phosphine has also some influence on the catalyst activity; the data reported in Table 3 seem to indicate that it is higher for catalysts based on cobalt complexes with less hindered phosphines. This fact could be interpreted by admitting an easier alkylation of the cobalt complexes with less hindered phosphines, with consequent formation of a larger number of active sites. Nevertheless it is also true that, in general, 1,3-diene polymerizations giving 1,2 polymers are much faster (larger kinetic constant *K<sub>p</sub>*) than those giving *cis*-1,4 polymers.

The different chemoselectivity exhibited, in the polymerization of butadiene, by the catalyst systems reported above can be interpreted on the basis of the diene polymerization mechanism proposed by Porri et al. [22]. Fig. 4 shows the well known scheme already reported in previous papers [22b]. *Cis*-1,4 units and 1,2 units can originate from the same allylic unit: if the new entering monomer inserts at C1 of the allylic unit, a *cis* 1,4 unit is formed; if the monomer inserts at C3, a 1,2

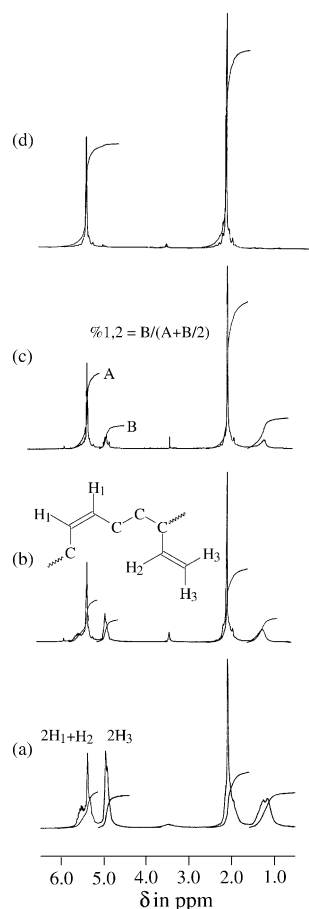


Fig. 3. <sup>1</sup>H NMR spectra of polybutadienes obtained with (a) CoCl<sub>2</sub>(P<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>-MAO (Table 3, run 2); (b) CoCl<sub>2</sub>(P<sup>*i*</sup>Bu<sub>2</sub>H)<sub>2</sub>-MAO (Table 3, run 4); (c) CoCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>-MAO (Table 3, run 6); (d) CoCl<sub>2</sub>(P<sup>*i*</sup>Bu<sub>2</sub>Me)<sub>2</sub>-MAO (Table 3, run 5).

unit is obtained. The type of ligand (only one is supposed to remain bonded to the metal in the active site since otherwise, in case of two ligands, we would have an electron in excess with respect to the rare gas (18e) rule [23]) can influence the reciprocal orientation of the allylic unit and the monomer; depending on the nature of the phosphine, the C1 or the C3 insertion can be favored with formation of *cis*-1,4 or 1,2 units, respectively. When the new incoming monomer has the same probability to insert at C1 (Fig. 4a) or C3 (Fig. 4b), an equilib-

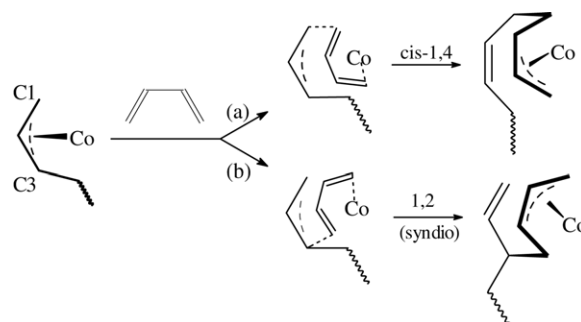


Fig. 4. Scheme of formation of *cis*-1,4 units vs. 1,2 units.

inary *cis*-1,4/1,2 (50:50) polymer can form, as happened for example in the polymerization of 1,3-butadiene with the system Fe(acac)<sub>3</sub>-Al(*i*Bu)<sub>3</sub>-(phen) [24].

#### 4. Conclusions

We have synthesized and characterized several phosphine cobalt(II) complexes; some of them are new and in some cases their crystal structures have been determined.

By polymerizing butadiene with these cobalt complexes associated with MAO, we have been able to obtain polymers having a microstructure ranging from predominantly 1,2 to essentially *cis*-1,4; these polymers, as it is well known, are the only two diene polymers of industrial interest.

Finally, the results obtained have also some mechanistic implications and have been interpreted on the basis of the diene polymerization mechanism previously proposed [22].

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#### Appendix A. Supplementary data

Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, bond distances and angles for CoCl<sub>2</sub>(PCy<sub>2</sub>H)<sub>2</sub> and CoCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>. This material is available free of charge via the Internet at <http://sciencedirect.com>.

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